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APPLICATION OF AN ANALYSIS PROTOCOL TO IDENTIFY ORGANIC COMPOUNDS NOT IDENTIFIED BY SPECTRUM MATCHING
Part 1: Text

by

Joan T. Bursey
Research Triangle Institute
Research Triangle Park, North Carolina 27709

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Project Officer

Walter M. Shackelford
Analytical Chemistry Branch
Environmental Research Laboratory
Athens, Georgia 30613

ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
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16. ABSTRACT

Industrial wastewater survey samples were analyzed for organic compounds not identified by spectrum matching. Analysis of the samples proceeded from an initial packed column GC/MS analysis for Priority Pollutants, through computerized spectrum matching for other compounds, to the present capillary column GC/MS analysis of a chosen set of sample extracts. Attention was focused on the spectra seen to occur frequently, yet not tentatively identified by spectrum matching. A plan for systematic study of these sample components was devised that included, in step-wise fashion, the use of high resolution gas chromatography, high resolution mass spectrometry, chemical ionization mass spectrometry with positive and negative ion detection, and Fourier transform infrared spectroscopy. Sample cleanup was used at all levels to mitigate interference. For 55 extracts in which components of interest were observed, accurate mass measurement was successfully used to generate chemical formulas in 35 cases. Of these, the results of 16 could be narrowed to one or two possibilities each. Tentative structures were proposed in six cases. Conclusions were: (1) that this type of compound/identification effort is very time and labor intensive, (2) that labor costs are high because highly trained and experienced personnel are required, and (3) that the amount of definitive information that can be obtained by application of any one of the analytical techniques discussed above ranges from minimal to extensive but that integration of information often is a complex problem.

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FOREWORD

Nearly every phase of environmental protection depends on a capability to identify and measure specific pollutants in the environment. As part of this Laboratory's research on the occurrence, movement, transformation, impact, anc control of environmental contaminants, the Analytical Chemistry Branch characterizes chemical constituents of water and soil.

Studies at this and other laboratories have shown that most compounds in survey analyses are not contained in present-day libraries of reference spectra. The ability to identify the most frequently occurring of these compounds requires the application of high resolution mass spectrometry, Fourier transform infrared spectroscopy, and other sophisticated analysis techniques. This report describes the application of a protocol for analyzing organics that are not represented in spectral libraries using effluent extracts from a variety of industries.

William T. Donaldson
Acting Director
Environmental Research Laboratory
Athens, Georgia

ABSTRACT

Industrial wastewater survey samples were analyzed for organic compounds not identified by spectrum matching. Analysis of the samples proceeded from an initial packed column GC/MS analysis for Priority Pollutants, through computerized spectrum matching for other organic compounds, to the present capillary column GC/MS analysis of a chosen set of sample extracts. Attention was focused on the spectra seen to occur frequently, yet not tentatively identified by spectrum matching. A plan for systematic study of these sample components was devised that included, in step-wise fashion, the use of high resolution gas chromatography, high resolution mass spectrometry, chemical ionization mass spectrometry with positive and negative ion detection, and Fourier transform infrared spectroscopy. Sample cleanup was used at all levels to mitigate interference. For 55 extracts in which components of interest were observed, accurate mass measurement was successfully used to generate chemical formulas in 35 cases. Of these, the results for 16 could be narrowed to one or two possibilities each. Tentative structures were proposed in six cases. Since the proposed compounds were not commercially available and the costs of synthesis were prohibitive, no further confirmation was made.

Conclusions were: (1) that this type of compound isolation/identification effort is very time and labor intensive, (2) that labor costs are high because highly trained and experienced personnel are required, and (3) that the amount of definitive information that can be obtained by application of any one of the analytical techniques discussed above (or of several of the techniques in succession) ranges from minimal to very high, but integration of all the information available is often not as simple as the analyst might wish.

This report was submitted in fulfillment of Contract Number 68-03-2867 by the Research Triangle Institute under the sponsorship of the U.S. Environmental Protection Agency. This report covers a period from December 1982 to February 1984, and work was completed as of February 1984.

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SECTION 1
INTRODUCTION

In June 1976, a Consent Decree was signed by EPA and several public interest groups (1) that set deadlines for EPA to promulgate regulations for treating industrial wastewater. Beginning in August 1977, some 4000 samples of plant influents and effluents were taken in 21 industrial categories to gather data on treatment processes. The analytical work was centered on 114 organic compounds and 15 inorganic substancecs called Priority Pollutants.

The sampling and analysis effort continued through August 1980. In 1979 an amendment to the Consent Decree was signed (2) that directed EPA, among other things, to determine by mass spectrum matching, the compounds in addition to the Priority Pollutants that might be present, chemically confirm those compounds of highest concentration and frequency of occurrence, and attempt to identify by other means significant components not identified by spectrum matching. Computerized spectrum matching of the raw GC/MS data was performed by the Athens Environmental Research Laboratory (ERL) (3). The chemical confirmation of matching results is the subject of a previous report (4).

The original computerized analysis aimed at deconvoluting and identifying all of the peaks of the chromatogram. A number of compounds, however, could not be identified by the computer but were observed frequently in several industrial categories. It was the objective of the second part of this program to endeavor to identify these compounds, or at least to arrive at a point where a structure could be postulated on the basis of available information. There were several steps to the screening process whereby the extracts were selected for analysis. A primary criterion was frequency of occurrence of a characteristic mass spectrum which could not be identified. A compilation was made of these mass spectra, ordered by frequency of occurrence. The spectra were screened by the Project Officer and the Principal Investigator, both experienced mass spectroscopists, and a few identifications which seemed obvious were made and some of the mass spectra were deleted from consideration for further analytical effort. Another major criterion for the selection of a mass spectrum for further analytical effort was an obvious indication of the presence of halogen, i.e., the presence of the isotopic clusters characteristic of the occurrence of halogen. The ultimate, and deciding, criterion was the availability of an extract where the unknown compound was present in a concentration sufficient to produce a mass spectrum of reasonable quality. If several industrial effluent extracts were available containing the unknown mass spectrum, the highest priority was given to the extract where the component was present at the highest concentration.

Once an extract had been selected for further analytical effort, the first step in the procedure was to repeat the analysis of the extract, using capillary gas chromatography instead of the packed column gas chromatography used in the first analysis. One obvious way in which computerized identification can fail is if the compound of interest coelutes with another compound from which successful deconvolution cannot be performed. So the first possibility was that the additional resolution afforded by capillary chromatography would allow straightforward identification of the compound of interest. In Phase II of the program, to a far greater extent than in Phase I, there were several instances where the compound of interest could simply not be found at all upon re-analysis of the extract. There were also many instances where the mass spectrum observed upon re-analysis was only similar to (not exactly the same as) the mass spectrum obtained on the original analysis. In these cases, the analytical effort on this extract was abandoned and another extract was selected in which the same mass spectrum was observed, if possible. When computerized library search was performed on the mass spectrum obtained from the capillary GC/MS assay, the "identification" was almost uniformly poor. The library parameters indicating quality of fit and, hence, the confidence level of the identification, were generally poor, indicating that a standard spectrum of the compound of interest was not present in the approximately 30,000 mass spectra of the NBS mass spectral library. In a few cases, the compound identified by the library did seem to be related to the mass spectrum of the compound of interest. In several cases, the only clue to the identification of the actual compound offered by the computerized library search was the fact that all of the first five possibilities contained nitrogen or oxygen. At this point in the analytical procedure, tentative structures could be assigned for a very few of the compounds and a few salient structural features could be discerned (i.e., presence of halogen, presence of an aromatic ring) but, for the most part, structural assignments could not be made.

More information was obviously required in order to make even tentative structural assignments. The most obviously desirable piece of structural information would be an elemental composition for the compounds of interest. This information could be obtained using the combination of capillary gas chromatography with accurate mass measurement techniques, and these analyses were performed for the vast majority of the extracts by Dr. T. Michael Harvey of Harvey Laboratories (Charlottesville, Virginia). With the information available from the elemental compositon, perhaps structural assignments could be made. Unfortunately, structural assignments could be made in only a very few cases. In many cases, many possibilities were presented as a result of the accurate mass measurement and there were no valid reasons for discarding some of the possibilities in favor of the others. So, in many instances, the accurate mass measurements added information but did not provide the definitive piece of information.

One of the questions which arose in the study of the mass spectra was whether molecular ion species were actually being observed. In an effort to resolve this question, chemical ionization techniques (in both the positive and negative mode) were applied to several of the extracts. In a very few cases, the use of chemical ionization techniques provided a key piece of information which allowed the postulation of a structure. It was a far more usual situation that the information provided by the chemical ionization techniques remained ambiguous and simply added additional pieces of information without aiding in the resolution of the structural questions.

Another analytical technique for which high hopes were held was the combination of the capillary gas chromatograph with Fourier transform infrared spectrometry. This technique holds many possibilities for structural identification (especially given an elemental compostion) because of its ability to specify functional groups. It would be essential in postulating a structure to differentiate between a ketone and an unsaturated alcohol, to assign relative positions of substituents on an aromatic ring, and to have access to many of the other types of information available from the infrared spectrometric technique. In additon, a Unacon automatic concentrator was used prior to the entry of the extract to the capillary gas chromatographic column in order to enhance the concentration of the component of interest. In its one successful application, the Unacon/capillary gas chromatograph/Fourier transform infrared spectrometer was outstandingly successful. However, several other attempts were completely unsuccessful for a variety of reasons. One of the main problems with the Fourier transform infrared technique is a severe lack of sensitivity, especially compared to mass spectrometric techniques. Sensitivity requirements of the Fourier transform infrared are of the order of micrograms, whereas many of the components of interest were simply not present at such high levels in the industrial effluent extracts. In addition, coupled gas chromatography with Fourier transform infrared spectrometry is an experimental technique at the Research Triangle Institute, and major difficulties were encountered in its application.

Many of the industrial effluent extracts were extremely complex, and a mass spectrum which was of relatively good quality was obtained only by application of sophisticated background subtraction techniques. Since most of the compounds of interest were polar, as evidenced by the results of the accurate mass measurement, a laboratory cleanup was attempted in the hopes that the component of interest would prove to be a major constituent in a fraction where it could be concentrated and subjected to other analytical determinations in an effort to assign a structure. The laboratory cleanup was generally very successful in the sense that the component of interest was most frequently isolated in a fraction which proved to be far less complex than the original industrial effluent extract. In a few cases, the component of interest could no longer be found at all after the application of cleanup techniques. In several cases, the component of interest proved to be only a minor constituent of a fraction and so was not a viable candidate for the application of other techniques. The cleanup techniques were, for the most part, quite successful in attaining their objective: they did remove polar from nonpolar constituents. However, the components of interest, for the most part, were present at such low concentrations in the original extract that no further analysis was possible.

In summary, then, industrial effluent extracts from a variety of types of industries were analyzed for the presence of a component of interest in hopes of being able to postulate a structure for this component of interest upon concatenation of information from a variety of analytical techniques. The ultimate objective was to confirm an identification by the synthesis of an authentic compound to allow confirmation of identification by co-injection.

SECTION 2

CONCLUSIONS

Several conclusions can be reached on the basis of evaluation of data obtained in the course of this phase of the program. The ability to perform capillary gas chromatogaphic analysis in conjunction with accurate mass measurement is invaluable. This combined technique should be more widely available and much more widely utilized. For an effort which is not proportionately much more than that required to perform the low resolution analysis, information about the atomic composition of the component of interest can be obtained and utilized in making further decisions in the chemical analysis.

An analytical technique that appeared very promising in prospect was the coupled technique of capillary gas chromatography/Fourier transform infrared spectrometry, prefaced by the Unacon automatic sample concentrator. With data available from accurate mass measurement, it was anticipated that the additional information about the nature of functional groups present in the molecule might produce not only general information on major structural features of the molecule, but in some cases, even specific isomeric assignments. Where the technique worked well, the outcome was all that could reasonably be anticipated. The structural features delineated by the infrared data integrated smoothly with the other information available (low resolution electron ionization mass spectrum and accurate mass measurement) to produce a structural postulation which narrowed the possibilities to one of two isomers, one more probable than the other.

Most of the analytical methods employed in this program have been found to be very labor-intensive, especially in the area of highly trained technical personnel (i.e., experienced degree-holders at Bachelor's Master's, and Ph.D. levels). The most efficient and cost-effective way to take advantage of the available mass spectrometric techniques is to have direct access to a single mass spectrometer where the original capillary gas chromatography/low resolution electron ionization mass spectrometric analysis can be performed. This analysis would then logically be followed immediately by re-injection of the sample and performance of the accurate mass determination, with subsequent re-injection(s) of the sample to take advantage of available chemical ionization techniques, if appropriate.

SECTION 3

RECOMMENDATIONS

The single major recommendation for optimizing this type of analysis is to have all applicable analytical techniques readily accessible, so that all information can be obtained in a very short chronological period and integrated quickly. It might also be helpful to other analysts doing similar types of analyses to gather the mass spectra of these components of interest which have been observed many times, in several types of industrial effluents, even though the compounds might be unidentified. If such a data base indicates that occurrence of a particular mass spectrum is frequent and that this mass spectrum is observed through a wide range of industrial effluents, then pursuit of definitive structural information would reasonably be assigned a higher priority, and perhaps then collection of sufficient sample would allow isolation of the component in relatively pure form by preparative analytical techniques. Access to micrograms of a relatively pure material would permit analysis by nuclear magnetic resonance and would certainly allow successful FT-IR analysis, and it should then be easier to formulate structural assignments.

SECTION 4

EXPERIMENTAL PROCEDURES

At the Mass Spectrometry Laboratory of the Research Triangle Institute, mass spectrometric analyses were performed on one of three gas chromatograph/mass spectrometer systems, the choice being dependent upon instrument availability. These systems were a Finnigan 3300 GC/MS/DS, a Finnigan 4021 GC/MS/DS, and a Finnigan 4500 GC/MS/DS. Electron ionization studies were performed on either the Finnigan 3300 or 4021. Chemical ionization studies, either positive or negative mode, were performed on the Finnigan 4500. Fused silica capillary columns were interchanged among the instruments.

CAPILLARY GAS CHROMATOGRAPHY/MASS SPECTROMETRY, WITH LIBRARY SEARCH

Sample extract concentrations were adjusted to appropriate levels for capillary analysis. Analytical conditions are shown in Table 4.1. The function of this initial capillary analysis was to establish the presence or absence of the component of interest. If the component of interest was not present, this fact was reported to the Project Officer so that another extract containing the same component could be selected for analysis, if possible. If the component was found, a mass spectrum of the best possible quality was obtained and a library search was performed on the Incos data system. In daily analysis, the first analysis of the day was always the system performance standard solution, in order to verify acceptability of the tune and acceptability of column performance parameters.

The library search used was the Incos system library search, with the NBS library of approximately 30,000 compounds as the data base. There were, in general, two observed outcomes of the library search. There were very few situations in which the library search produced a compound identification of acceptable quality. The library simply did not contain reference spectra of most of the components of interest.

Table 4.1. Instrumental Parameters

<table>
<tr><th></th><th>Finnigan 3300</th><th>Finnigan 4021</th></tr>
<tr><td></td><td colspan="2">Gas Chromatography Parameters</td></tr>
<tr><td>Column</td><td colspan="2">60 m OV-101 wide-bore thick film fused silica capillary.</td></tr>
<tr><td>Initial Temperature</td><td colspan="2">30°C</td></tr>
<tr><td>Minutes Isothermal</td><td colspan="2">6 minutes at 75°C</td></tr>
<tr><td>Programming Rate</td><td colspan="2">4°C/min</td></tr>
<tr><td>Maximum Temperature</td><td colspan="2">270°C</td></tr>
<tr><td>Column Flow</td><td>1.2 mL/min He</td><td>1.6 mL/min He</td></tr>
<tr><td>Injector Temperature</td><td>250°C</td><td>270°C</td></tr>
<tr><td>Injection Mode</td><td>Splitless for 60 sec, then ~10:1 split</td><td>Splitless for 24 sec, then 7.5:1 split</td></tr>
<tr><td>Column</td><td colspan="2">60 m Carbowax 20 M wide-bore thick film fused silica capillary.</td></tr>
<tr><td>Initial Temperature</td><td colspan="2">30°C</td></tr>
<tr><td>Minutes Isothermal</td><td colspan="2">6 minutes at 75°C</td></tr>
<tr><td>Programming Rate</td><td colspan="2">4°C/min</td></tr>
<tr><td>Maximum Temperature</td><td colspan="2">220°C</td></tr>
<tr><td>Column Flow</td><td colspan="2">1.2 mL/min He</td></tr>
<tr><td>Injector Temperature</td><td>250°C</td><td>230°C</td></tr>
<tr><td>Injector Mode</td><td>Splitless for 60 sec, then ~10:1 split</td><td>Splitless for 24 sec, then 2.5.1 split</td></tr>
<tr><td></td><td colspan="2">Mass Spectrometer Parameters</td></tr>
<tr><td>Transfer Line/Separator Oven</td><td colspan="2">270°C</td></tr>
<tr><td>Ionization Energy</td><td colspan="2">70 eV</td></tr>
<tr><td>Emission Current</td><td colspan="2">0.5 mA</td></tr>
<tr><td>Mass Range</td><td colspan="2">40-500 daltons</td></tr>
<tr><td>Scan Speed</td><td>2 sec/cycle</td><td>1 sec/cycle</td></tr>
</table>

The best possible outcome of the library search was usually a consistency in type of compound appearing as the top five choices: namely, if all of the top five choices contained oxygen or nitrogen, there could be a reasonable amount of certainty that the compound of interest could be characterized as oxygen-containing or nitrogen-containing. In some cases, it could be seen that, although the specific mass spectrum of the compound of interest was not contained in the data base, the compound of interest could be characterized as a member of a family, and mass spectra of some members of this family were contained in the data base. The other possible outcome of the computerized library search was a complete dearth of information: there was no consistency in the types of compound listed as top choices, nor was there any meaningful information obtained about the family to which the compound might belong.

CAPILLARY GAS CHROMATOGRAPHY WITH ACCURATE MASS MEASUREMENT

The capillary gas chromatography for accurate mass measurement was performed under the same conditions as those shown in Table 4.1 for the Finnigan 4021 GC/MS system. The accurate mass measurements were performed on a VG Micromass 7070HS, at a resolving power of 2000, with a 5% valley. Ionizing energy was 70 eV, 200 μA trap current, a source temperature of 210°C, and a transfer line temperature of 275°C. The scan speed was 700 msec/decade, from m/z 550-20, with a 500 msec reset time. C_2I_4 was used as a secondary reference. Data were taken and processed on a VG 2035 data system. As a routine analytical procedure, the industrial effluent extract was analyzed first at low mass spectrometric resolution in order to verify the presence of the component of interest. When the component of interest had been located, the mass spectrometer was set up for higher resolving power, and the accurate mass measurement was made upon re-injection of the sample. Each extract was spiked with 2-fluorobiphenyl as a standard, and an accurate mass measurement was always made of this standard in order to verify proper operation and stability of the instrument. Data were obtained as a table of calculated masses and compositions, usually for most of the major peaks of the mass spectrum of the component of interest. The data were examined by the Project Director, and some of the possibilities were eliminated where there were reasonable grounds to do so. Some of the reasons to eliminate a given composition from further consideration as a possibility were: incorrect number of nitrogen atoms (an odd-mass molecular ion necessitates an odd number of nitrogen atoms), chemically impossible composition (the computer simply calculates numerically plausible combinations of atoms, with no consideration of chemical logic), or lack of a fragment ion composition corresponding to a logical transition (for example, if a fragment ion is present which corresponds to a loss of 15 mass units, this loss must correspond to a methyl radical; if there is no ion present in the mass table with a composition of $M-CH_3$, the composition postulated for M cannot be correct and must be eliminated from further consideration). At this point, the possibilities could occasionally be narrowed down to one and a tentative structure postulated. Sometimes there was only one possibility resulting from the accurate mass measurement, but a definitive structure could still not be suggested. Sometimes, even after elimination of possibilities for the reasons described above, there were still multiple candidate compositions with no logical reason to choose among them. This is the point at which a decision on further analytical operations is very difficult. Invariably, there is not enough of the component of interest present to allow isolation and, hence, an opportunity for better characterization by other spectroscopic techniques. The only possibilities for further analytical operations would require the use of some technique where an interface with the chromatographic separation method is feasible. The problem at this point begins to take on the aspects of a minor research program. It is possible that capillary gas chromatography interfaced to the Fourier transform infrared spectrometer will yield meaningful information, but there are concentration problems to overcome and the additional uncertainty of having not even a tentative structural assignment at this point. It is also possible that chemical ionization techniques may yield some meaningful information, but not the routine types of chemical ionization analysis usually done to establish the presence of a molecular ion. The meaningful information to be obtained from chemical ionization mass spectrometry at this point concerns the finer points of ionization chemistry, namely reactions specific to functional groups, requiring a variety of techniques and a wide variety of reagent gases. It is possible that a battery of chemical ionization analyses might be performed with a compound of completely unknown structure and no meaningful specific structural information extracted from any of the analyses.

CAPILLARY GAS CHROMATOGRAPHY WITH CHEMICAL IONIZATION MASS SPECTROMETRY (POSITIVE AND NEGATIVE MODES)

Chemical ionization analyses were performed in the pulsed positive/negative chemical ionization mode. The instrument used was a Finnigan 4500 GC/MS/DS. Capillary columns and conditions correspond to those used on the Finnigan 4021 and reported in Table 4.1. The reagent gas was methane, at a source pressure of 0.7 torr and an analyzer pressure of 2×10^{-5} torr. The source temperature was 120°C, with an electron energy of 100 eV and an emission current of 0.2 mA. The scan cycle was 1 sec, with a scan range of 90-550 daltons. The multiplier was operated at 1300 V, with the amplifier at 10^{-7} A/V. Chemical ionization analyses were attempted in only a few cases, and the success rate (success being defined as the extraction of meaningful information from the data obtained) was not very high. The major circumstance in which chemical ionization analysis was found to be useful was when there was doubt whether the species observed in the mass spectrum represented a molecular ion. In this case, a species of mass M was observed in the electron ionization mass spectrum and the ion was observed at $(M+1)^+$ in the chemical ionization mass spectrum. With this type of information, the investigator can be reasonably confident of the molecular weight of the compound of interest. In some instances, the use of chemical ionization techniques reveals an ion which was not previously observed in the electron ionization mass spectrum, with no clear and obvious relationship to the other ions of the electron ionization mass spectrum. In a case such as this, the results of the chemical ionization analysis are difficult to interpret, and integration of the results of several different types of chemical ionization data might be helpful in determining a molecular weight or assigning structural features. Chemical ionization techniques (pulsed mode) were applied unsuccessfully to the analysis of highly halogenated alkanes and alkenes in an effort to obtain an indication of molecular weight and/or number of halogen atoms present in the molecule. Information of value was obtained, namely, that the highest mass ions observed under electron ionization conditions represented neither the molecular weight of the compound nor the actual number of halogen atoms present in the molecule. However, the ions observed in either positive or negative chemical ionization still were not characteristic of molecular weight although these ions indicated the presence of more halogen atoms than the electron ionization data.

USE OF LABORATORY CLEANUP PROCEDURES IN REMOVING BACKGROUND MATERIAL

In an effort to minimize the contribution of high levels of background material (mostly hydrocarbons) to the mass spectra obtained for the components of interest, several extracts were subjected to laboratory cleanup procedures. The components of interest were polar molecules and it was a reasonable anticipation that these polar materials could be separated from nonpolar materials (especially hydrocarbons) and thus be characterized more easily. In fact, some of the polar materials could not be observed at all over the intense hydrocarbon envelope.

Reagents

All samples were methylene chloride extracts of aqueous industrial effluents provided by the Environmental Protection Agency. These extracts had been stored in sealed glass ampules at -20°C for periods ranging from two to four years before cleanup and analysis. All solvents used were distilled-in-glass grade. Chromatography columns were prepared from Fisher reagent grade silica gel deactivated at 105°C for 14 h then reactivated by equilibrating for 2 h with 14 mL of reagent water per 100 g. Neat materials for standards were purchased commercially and checked for purity by gas chromatography with flame ionization detection prior to use.

Procedure

Prior to fractionating any samples, the activity of the sorbent was verified using a chromatography column containing 5.00 ± 0.05 g of dry activated silica gel. A 10 mL aliquot of a standard solution containing naphthalene (0.5 mg) and anthracene (1.0 ng) was loaded onto the column and allowed to drain through until the solvent reached the silica gel. The column was then eluted with an additional 10 mL of solvent. The two eluants were combined, diluted to 15 mL with pentane and analyzed by gas chromatography with flame ionization detection, to determine the recovery of the two standards. The amount of silica gel in the column was adjusted to give recoveries between 50 to 70% for both standards.

A fresh column was then prepared for each sample to be fractionated. Sample extracts were solvent-exchanged into pentane by diluting to 10 mL with pentane. Materials in the sample extracts which were not soluble in pentane often precipitated during this procedure. The entire sample was loaded onto the column and allowed to drain through until solvent had just reached the top of the sorbent material. An additional 10 mL of pentane was eluted through the column and the two eluants were frequently combined as Fraction 1. The column was then eluted with 20 mL of 20% methylene chloride, 80% pentane (v/v) to generate Fraction 2. Each time a new solvent was used the original sample vial was rinsed with three 2 mL portions of that solvent to remove materials which were not soluble in pentane and to assure that all sample material was transferred to the column. All fractions were concentrated to 1 mL and then spiked with 4-fluoro-2-iodotoluene to serve as an external standard for mass spectrometric analysis and deuterated standards to check recovery. Extracts were stored at 0°C until GC/MS analysis.

Upon subsequent analysis by capillary GC/MS, one or two of the fractions were examined for the presence of the component of interest. Since the components of interest were expected to be polar, based on the results of the accurate mass measurement, it was usually not necessary to examine all three fractions since two of the fractions were non-polar. Major peaks in each fraction analyzed were characterized by computerized library search in order to obtain an indication of the types of compounds which were isolated from the original extract into the particular fraction and to establish the presence of the component of interest in a given fraction. Results were mixed. There were several cases where the component of interest could not be found after sample cleanup and fractionation. When the component of interest could be found, it was usually in the polar fraction. However, the component of interest was often only a minor constituent of the polar fraction and, although obtaining a mass spectrum free of extraneous ions was therefore simpler, the fractionation procedure did not in these instances aid in making the component of interest more amenable to the application of other analytical techniques. The cleanup process is, for the most part, efficient, effective, and not very costly to apply, in that relatively nonskilled junior laboratory personnel can be trained to execute the procedure and can thereafter process several extracts at a time, limited only by the amount of equipment available.

APPLICATION OF FOURIER TRANSFORM INFRARED (FT-IR) SPECTROMETRY WITH CAPILLARY GAS CHROMATOGRAPHY AND UNACON

In the case of several extracts, pooling of information from several sources such as low resolution mass spectrometry, accurate mass measurement, chemical ionization mass spectrometry, and interpretation of the various types of data either produced a tentative structure or suitably narrowed the possibilities so that information concerning the nature of the functional group(s) present in the molecule would have been extremely helpful in arriving at a final structure. The obvious technique for determining the nature of functional groups in a polar molecule would be infrared spectrometry, especially Fourier transform infrared spectrometry. However, since the components of interest in the industrial effluent extracts are present as a part of a very complex matrix, a prefatory separation technique with as much resolution as possible would be extremely desirable in producing definitive information. The capillary gas chromatograph interfaced to the Fourier transform infrared spectrometer provides a powerful analytical tool, but there are valid questions about sensitivity for the coupled technique. In order to use the technique to its full advantage, a Unacon 810A was interfaced to the capillary gas chromatograph to increase injection volume and thereby lower detection limits.

Use of the Unacon 810A

The Unacon 810A is a commercial injection system which uses a preconcentration technique to increase injection volume and thereby decrease analytical detection limits. In operation, the Unacon removes solvent prior to injecting analytes onto the chromatographic column. Organic compounds are retained and concentrated on two sorbent traps in series. For ultimate analysis, the organic compounds are thermally desorbed onto a capillary column for analysis by gas chromatography/Fourier transform infrared spectrometry. The first of the two sorbent traps has a large internal diameter to retain organics from a large solvent volume (typical injection volumes are 50-100 µL) over an extended trapping period. The second of the sorbent traps has a smaller internal diameter to allow efficient desorption onto the capillary column at low gas flow rates.

Apparatus--

The Unacon 810A system was interfaced to a Varian 3700 gas chromatograph using a fused silica capillary column. The capillary column was attached directly to the transfer line of the Unacon 810A which was wrapped with heating tape and heated to 165°C to prevent condensation of the less volatile organics during transfer. The Unacon 810A system was equipped with a large-bore trap (6.35 mm OD, 2.54 mm ID x 20.3 cm in length) containing Tenax GC® and glass beads and a small-bore trap (6.35 mm ID, 0.9 mm ID x 20.3 cm in length) also containing Tenax and glass beads as sorbent material. Previous experience with evaluation of the Unacon 810A has demonstrated that the poorest relative injection efficiencies are obtained for the higher molecular weight polynuclear aromatic hydrocarbons and some very polar compounds. For some compounds, several injections of the same solution are required before a stable chromatographic response is achieved. These properties of the Unacon could cause problems in the analysis of components of interest from the industrial effluent extracts: from the accurate mass measurements the highest probability is that the compounds of interest are polar, many of them highly polar.

A Varian 3700 gas chromatograph was used to vaporize and analyze the industrial effluent extracts. The column used to obtain GC/Fourier transform infrared spectrometry data was either a 60 m wide-bore chemically bonded DB-1 or a 60 m wide-bore chemically bonded Carbowax 20 M fused silica capillary column. The carrier gas was helium at a flow rate of approximately 3.25 mL/min. All injections to the gas chromatograph were done with a Unacon 810A automatic sample concentrator. The effluent resulting from an approximately 50 μL injection to the Unacon was passed through the gas chromatograph and transferred directly from the capillary column to the Nicolet light pipe (Figure 4.1). The effluent from the light pipe was transferred back to the flame ionization detector of the 3700 gas chromatograph for secondary detection.

The temperature of the injector block, column oven, transfer lines, and light pipe were interdependent. The injector block and column to light pipe transfer line were set approximately 10°C above the maximum column oven temperature. The light pipe was kept 10-20°C above the injector and column to light pipe transfer line to prevent condensation of any compounds within the light pipe. The light pipe to flame ionization detector transfer line was kept approximately 10°C higher than this transfer line. A typical GC/FT-IR temperature profile is given in Table 4.2.

A Nicolet 7199 Fourier transform infrared spectrometer was used with a Model 7001P Michelson interferometer, a high energy cooled glow bar source, a heated 0.3 mm ID x 42 cm (3 cm^3) gold-plated light pipe, and a 4000 to 800 cm^{-1} range liquid nitrogen cooled Mercury-Cadmium-Telluride detector, with related optics. The entire system was enclosed within a sealed nitrogen- purged enclosure.

The spectrometer was controlled by a Nicolet 1180 data system with 40K solid state memory interfaced to the spectrometer by a high precision 15 bit analog-to-digital converter. Twenty bit spectral words were acquired and stored on a Diablo 44B dual density, dual disk memory system. Long term data storage was accomplished using a Kennedy 9000 9-track, 800 bits-per-inch, 37 inches-per-second tape deck.

The operating parameters of this instrument are presented in Table 4.3. The triangular apodization function was used to generate a spectrum similar to one that would be obtained using a grating IR spectrometer. Also, 4096 data points were collected and 8192 points were transformed to give 4 cm^{-1} resolution spectra.

A standard solution was analyzed every day that data were acquired. A 3 μg/μL isobutylmethyl methacrylate (IBM) and 3 μg/μL of 3-methyl-2-butanone standard solution was used as a reference standard.

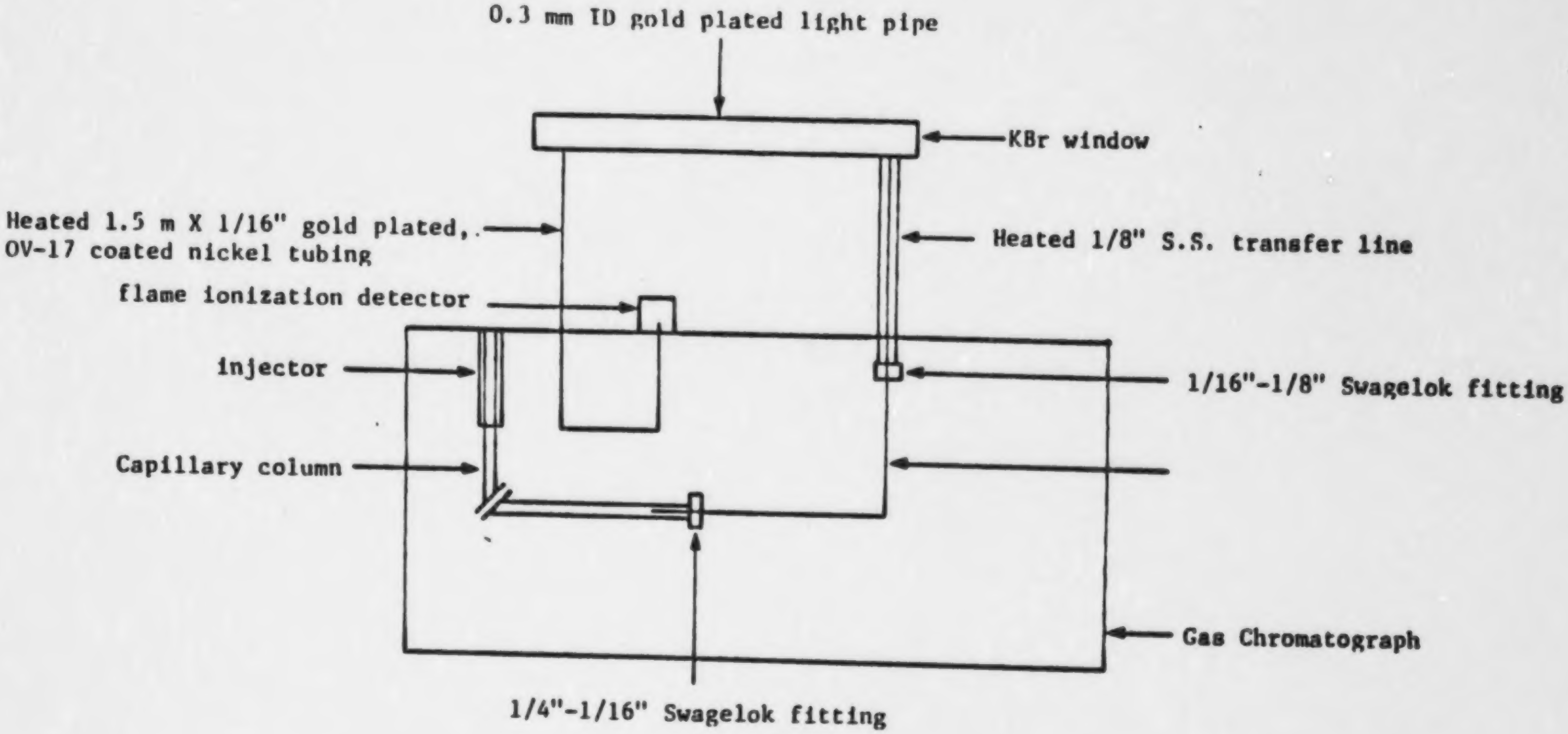

0.3 mm ID gold plated light pipe
KBr window
Heated 1.5 m X 1/16" gold plated, OV-17 coated nickel tubing
Heated 1/8" S.S. transfer line
flame ionization detector
injector
1/16"-1/8" Swagelok fitting
Capillary column
Gas Chromatograph
1/4"-1/16" Swagelok fitting

Figure 4.1. Schematic of GC/FT-IR interface.

Table 4.2. Typical GC/FT-IR Temperatures

Injector Temperature	260°C
Column Oven Temperature Program	100°C to 240°C at 4°C/min
Column to Light Pipe Transfer Line Temperature	240°C
Light Pipe Temperature	260°C
Light Pipe to FID Transfer Line Temperature	260°C
FID Temperature	270°C

Table 4.3. GC/FT-IR Data Acquisition Parameters

Spectrometer	Nicolet 7199
Infrared Detector	MCT
Apodization Function	Triangular
Number of Data Points	4096
Number of Transform Points	8192
Aperture Size	Fully Open
Interferogram Correlation	Low
Mirror Velocity	35 cm/sec
High Pass Filter Setting	1
Low Pass Filter Setting	6
File Size (points)	5632
Amplifier Gain	2
Number of Data Scans Compared per Stored File	4
Number of Background Scans	64
Starting Spectrum Wave number	4000
Final Spectrum Wave number	800
Cell Length	42 cm
Cell Volume	3 mL

Observations

Fourier transform infrared spectrometry, especially interfaced to the capillary gas chromatograph, is a useful tool in the identification of hazardous chemicals. Infrared spectroscopy can, for example, clearly differentiate between the four trichlorophenol isomers, whereas mass spectrometry cannot. There are, however, some limitations on the infrared technique, especially with the chromatographic interface. Compounds which cannot be chromatographed cannot be analyzed by the combined method. Compounds with a very high boiling point which elute late in the chromatogram exhibit a broad shallow peak shape and will not show a high absorbance in the infrared. Thermally unstable compounds are not compatible with the GC/FT-IR technique. The single most important factor determining the quality of the FT-IR analysis and the limit of detection is the extinction coefficient, which is an intrinsic property of the compound. Compounds which have a low extinction coefficient will not be detected by the FT-IR. In the case of the analysis of the unknown components of industrial effluent extracts, the extinction coefficients will, of course, be completely unknown, as will boiling points. However, a reasonable degree of thermal stability and volatility can be inferred from the fact that the compound can be successfully analyzed by gas chromatography. This information alone, however, is not sufficient for prediction of successful capillary GC/FTIR analysis.

SECTION 5

RESULTS AND DISCUSSION

A flow chart scheme from the original proposal was adhered to very strongly in the second phase of this program. This flow chart is presented in Figure 5.1. Various points in the flow chart are labeled A, B, ... etc., and progress was evaluated in relation to these points.

Point A (capillary GC/low resolution EIMS analysis. Pertinent component still observed?) was the starting point for each industrial effluent extract. There were three possible outcomes from this analysis: 1) the component of interest was observed (progress to points B and C); 2) the component of interest was not observed (analysis of the pertinent industrial effluent extract was abandoned and another extract was substituted, if available); or 3) a mass spectrum only similar to (not exactly corresponding to) the component of interest was observed (same outcome as (2), above). At point B (sufficient GC separation?), the GC separation did not prove crucial to the capability of observing a mass spectrum for the component of interest. Using computerized background subtraction techniques, it was possible to deconvolute mass spectra even in the face of severe coelution problems. However, several extracts (see point E) were subjected to cleanup procedures because of their extreme complexity. In the majority of these cases, the cleanup procedures were successful in their primary goal, to separate polar from nonpolar material. In several instances, polar materials could be observed and characterized in a cleaned-up extract fraction where these same materials could not be observed at all over a very high background consisting mostly of hydrocarbons. Since most of the compounds of interest were polar (some of them containing several polar functional groups), the laboratory cleanup technique has proven to be extremely useful in removing these components from a hydrocarbon background in order to facilitate their characterization. A well-resolved component can produce a much cleaner mass spectrum

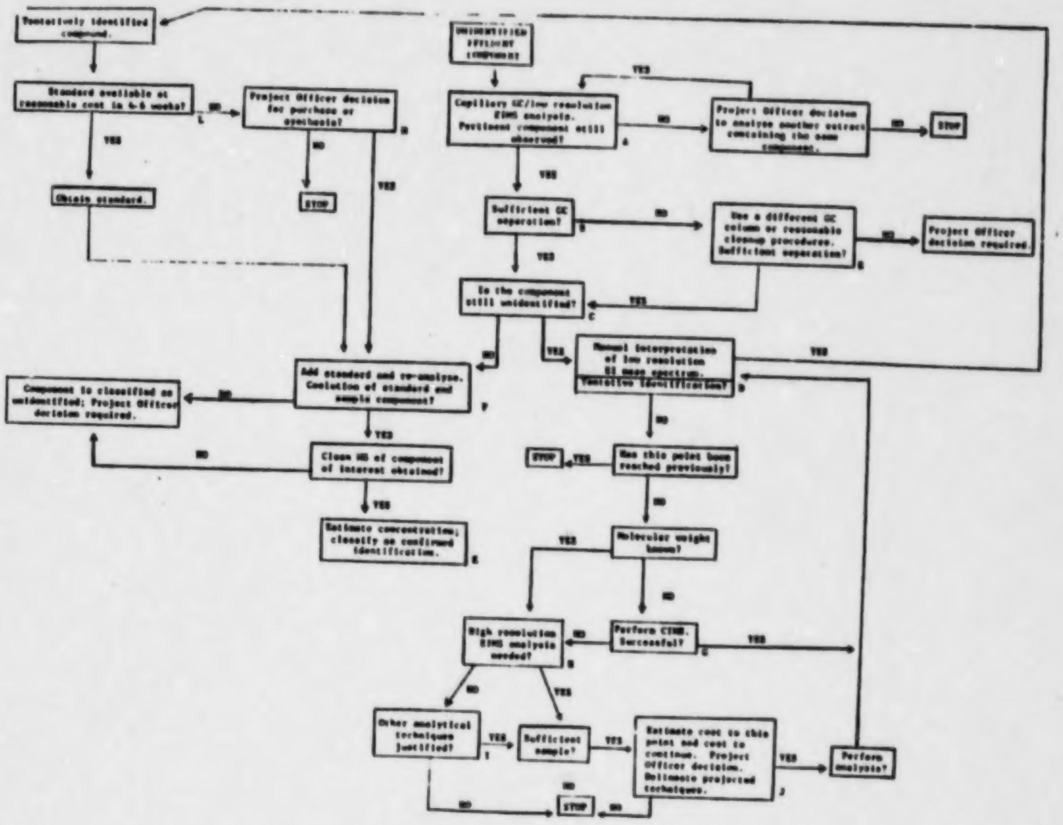

Tentatively identified compound.
Standard available at reasonable cost in 4-6 weeks?
NO
L
Project Officer decision for purchase or synthesis?
M
NO
STOP
YES
YES
Obtain standard.
UNIDENTIFIED EFFLUENT COMPONENT
Capillary GC/low resolution EIMS analysis. Pertinent component still observed?
A
NO
Project Officer decision to analyze another extract containing the same component.
YES
NO
STOP
YES
Sufficient GC separation?
B
NO
Use a different GC column or reasonable cleanup procedures. Sufficient separation?
E
NO
Project Officer decision required.
YES
YES
Is the component still unidentified?
C
NO
YES
Manual interpretation of low resolution EI mass spectrum. Tentative identification?
D
YES
Add standard and re-analyze. Coelution of standard and sample component?
F
NO
Component is classified as unidentified; Project Officer decision required.
YES
Clean MS of component of interest obtained?
NO
YES
Estimate concentration; classify as confirmed identification.
K
NO
Has this point been reached previously?
YES
STOP
NO
Molecular weight known?
YES
NO
Perform CIMS. Successful?
G
YES
NO
High resolution EIMS analysis needed?
H
NO
YES
Other analytical techniques justified?
I
YES
Sufficient sample?
YES
Estimate cost to this point and cost to continue. Project Officer decision. Delineate projected techniques.
J
YES
Perform analysis?
NO
NO
STOP
NO

Figure 5.1. Flow Chart for Ab Initio Compound Identification

without the use of extensive computerized background subtraction. Also, in the event that a technique such as preparative gas chromatography were to be applied in an effort to isolate a component, a cleaner chromatogram would be very helpful. In terms of the goals of this program, however, the laboratory cleanup procedures, although generally successful, did not facilitate identification. If the computerized techniques produce a spectrum of reasonable quality, then the ability to identify the component from the mass spectrum is a function of either manual interpretation of the mass spectrum or use of a library or other compendium of mass spectra which contains the mass spectrum or one very similar to it. The major problem with using the NBS library for identification of these components of interest proved to be that the library did not contain the mass spectrum of the component of interest, although in some cases related compounds were observed. The cleaner fraction should, however, be useful for application of other analytical techniques.

Therefore, at point C (Is the component still unidentified?), the answer was almost invariably that the component was still unidentified. At point D (Manual interpretation of low resolution EI mass spectrum: tentative identification?), there were some structural features which could be elucidated but only rarely could a postulation of a complete structure be made. For all practical purposes, point F (Add standard and reanalyze. Coelution of standard and sample component?) was never reached. Only once was a standard obtained commercially corresponding to a postulated structure; in this instance, elution times of standard and component of interest did not correspond. At point L (Standard available at reasonable cost in 4-6 weeks?), the standards to correspond to tentative structures were found to be unavailable commercially. At point M (Project Officer decision for purchase or synthesis.), synthesis was considered at one time where the postulated structure seemed to be narrowed down to one possible isomer, but the projected cost of $2,000-3,000 for a single compound was prohibitive, and no synthesis was performed.

At point G (Perform CIMS. Successful?), chemical ionization mass spectrometry (in both positive and negative mode) was performed for a number of samples. One of the primary instances of application of the chemical ionization technique was the occurrence of components of interest which appeared to be highly halogenated alkanes and alkenes. These compounds do not produce molecular ions (or any species characteristic of molecular weight) under electron ionization conditions. The mass spectrometric literature does not show instances of successful application of chemical ionization techniques to these types of compounds, but an effort was made (in both positive and negative mode) to see if any information could be obtained. Often, the chemical ionization data showed that the ionic species observed in the electron ionization mode contained more halogen (primarily chlorine, although bromine was observed in some instances) and quite probably more carbon than could be deduced from the electron ionization mass spectra alone. However, there was still no assurance that a mass spectrum in any mode showing ions characteristic of the molecular weight of these types of compounds had been obtained. In a few cases, application of chemical ionization techniques produced a species that was consistent with a protonated molecular ion corresponding to a tentative structure, and the chemical ionization data provided useful information in the postulation of a tentative structure. In some instances, no definitive information whatsoever was obtained from the application of chemical ionization techniques.

Point H (High resolution EIMS analysis needed?) proved to be a crucial point in the decision-making process, and the high resolution EIMS technique was applied to most of the extracts. The technique as actually applied required capillary gas chromatographic analysis followed by accurate mass measurement. Attempts to use high resolution techniques without the benefits of the preceding capillary separation were uniformly unsuccessful: the ions characteristic of the components of interest could not usually be discerned over the background. Using accurate mass measurement techniques with capillary separation allowed the accurate mass measurement to be done for several peaks of the mass spectrum. Thus, in several cases, it was possible to screen some of the potential compositions given for ions and eliminate possibilities which, for instance, did not have logical transitions for some of the peaks in the mass spectrum. For example, if the mass spectrum showed an $(M-15)^+$

species, this ion could arise only from the loss of a methyl radical, and if accurate mass measurement did not show this loss for a suggested precursor structure, this ion could be eliminated from further consideration as a possible elemental composition. Also, the accurate mass measurement proved invaluable in deciding whether or not the component of interest was polar, and would therefore be amenable to use of laboratory cleanup techniques. The accurate mass measurement data also enlarged the possibilities for postulation of structure. Beyond the salient points which could be deduced from the low resolution mass spectrum, there were often large portions of the molecular structure for which no postulations at all could be made or there were so many possibilities that no meaningful decision could be made. Usually the accurate mass measurement technique served effectively to limit the possibilities, although often there was still not an ability to make specific structural postulations. In the case of this program, the Mass Spectrometry Laboratory of the Research Triangle Institute does not presently possess the capability of performing capillary gas chromatographic analysis with accurate mass measurement, so these analyses were performed under a subcontract by one of the few laboratories in the United States which possesses this capability (Harvey Laboratories; Charlottesville, Virginia). The information gained was invaluable, but the mechanism of operation was unsatisfactory for a number of reasons. The ideal situation would be to have the required capability in-house, so that the Project Director could interface directly and immediately with the person performing the actual analysis. When this direct interaction is possible, a quick decision can be made whether to do chemical ionization analysis with the added capability of accurate mass measurement. In the subcontract situation, data turnaround was extremely slow, and a review by the Project Director was necessary before chemical ionization procedures could even be considered. The net result of the long delays was that, in spite of capability to perform capillary gas chromatography/chemical ionization mass spectrometry with accurate mass measurement, this technique was not used and its benefits could not be assessed. If the capability were available in-house, the data could be reviewed, a decision made, and the sample reinjected immediately under chemical ionization conditions in order to provide efficient, timely, and cost-effective utilization of the potential of the technique. The ability to perform capillary gas chromatographic analysis followed by accurate mass measurement is invaluable. This technique should be more widely available and much more widely utilized. For an effort which is not proportionately much more than that required to perform the low resolution analysis, information about the atomic composition of the component of interest can be obtained and utilized in making further decisions in the chemical analysis.

At point I (Other analytical techniques justified?), there are several major decisions to be made. One criterion for deciding if other analytical techniques are justified is a cost-benefit analysis: relative to the cost in time and dollars of performing the proposed analysis, is the structural information to be gained from the application of the technique proportionate? For example, one technique which had been considered for possible use in the earlier stages of the program was nuclear magnetic resonance (nmr). The possible benefits to be attained from the application of this technique are major: nmr can provide definitive structural information which, in conjunction with the information available from the application of capillary gas chromatography/accurate mass measurement, can produce definite structure assignments. However, data obtained early in the program precluded the use of nmr techniques: concentrations of components of interest were simply not high enough to fulfill the sample requirements of the nmr technique.

One analytical technique which held out high possibilities, however, was the coupled technique of capillary gas chromatography/Fourier transform infrared spectrometry. Again, with the data from accurate mass measurement available, it was anticipated that the additional information about the nature of functional groups present in the molecule might produce not only general information on major structural features of the molecule but, in some cases, even specific isomeric assignments. There is, however, one drastic limitation of the Fourier transform infrared technique: sample requirements are high, often in the microgram range, as opposed to the nanogram or even picogram range which is usually accessible to mass spectrometric techniques. For this reason, an attempt was made to interface the Unacon automatic sample concentrator to the capillary gas chromatograph to enhance the concentration of the component of interest in the industrial effluent extract. Also, the potential candidates for the use of Fourier transform infrared techniques were selected very carefully to insure that the component of interest was a major constituent in the chromatogram and thus enhance the probability of success. Where the technique worked well, the outcome was all that could reasonably be anticipated. The structural features delineated by the infrared data integrated smoothly with the other information available (low resolution electron ionization mass spectrum and accurate mass measurement) to produce a structural postulation which narrowed the possibilities to one of the two isomers, one more probable than the other. Other attempts to apply the technique were not successful, probably for a variety of reasons. The use of the coupled technique (Unacon, capillary gas chromatograph, Fourier transform infrared spectrometer) is experimental at the Research Triangle Institute, and there are numerous practical difficulties associated with performing assays of this nature. In spite of the fact that capillary columns were exactly the same as those used in the mass spectrometric analysis and carrier gas flows were nominally the same, efforts to correlate the information obtained by the two techniques suggest that perhaps the gas flows obtained were too low in the infrared system and the analyses were not prolonged sufficiently to observe the components of interest. Use of the Unacon made the technique very costly in terms of sample quantity required, so there was not enough sample to allow multiple attempts at analysis to be made. There is still the possibility, also, that even with the Unacon, the concentration of the component of interest in the extract was not sufficiently high to allow successful analysis. The use of capillary gas chromatography coupled with the Fourier transform infrared technique (especially if the Unacon can be used successfully to effect a concentration of the component of interest) is an extremely exciting technique in terms of the potential it offers for making structural assignments. The present requirements for successful application of the technique to problems of environmental significance include some extensive developmental efforts with the present system, better techniques for assuring that the mass spectrometer and the infrared spectrometer are indeed analyzing the same component, and, possibly, changing the system to take advantage of state-of-the-art developments in this area of analysis. Manufacturers are currently advertising use of capillary gas chromatography coupled with infrared techniques, although sensitivity requirements are still higher than those performing environmental analysis with its associated low concentrations of components of interests would like them to be.

In summary, the following analytical methods were applied during this research program:

(1) capillary gas chromatography with low resolution mass spectrometry. This analysis was essential as a first step in this program, in the absence of any data to indicate whether the component of interest could still be observed in the industrial effluent extract after extensive handling and a long period of storage;

(2) capillary gas chromatography with accurate mass measurement. This technique was probably the single outstandingly information-rich technique applied. If the coupled capillary chromatography/accurate mass measurement technique were readily accessible, this would reasonably be the first mode of analysis used after the preliminary low resolution analysis to establish the presence of the component of interest to allow a narrowing of the window for accurate mass measurement, so that a prohibitive amount of data is not collected in accurate mass measurement.

(3) capillary gas chromatography/chemical ionization mass spectrometry. An assessment of the utility of this technique would tend to be somewhat severe--where chemical ionization is useful, it tends to be extremely useful. However, there are many possible components of interest to which chemical ionization (either positive or negative mode) cannot be applied successfully because the reaction chemistry is not favorable. There are many other situations where chemical ionization can be applied but evaluation of the information is difficult: since the analyst does not know what his component of

interest might be when he uses the techniques of chemical ionization, it is sometimes impossible to assess whether protonation, addition of a hydrocarbon group, or some type of addition/ cleavage chemistry (all possible with various types of chemical ionization) has occurred. In the absence of a knowledge of the chemical ionization chemistry, unwarranted assumptions about the observation of a protonated molecular ion (and, hence, the molecular weight) of the component of interest might be made and the chemical ionization information might be extremely misleading.

4) capillary gas chromatography/Fourier transform infrared spectrometry. This coupled technique was prefaced by a Unacon automatic concentrator, in an effort to enhance the sensitivity of the technique. The information available from the application of the coupled technique was the nature of functional groups to be found in a molecule. The concatenation of this information with the information available from accurate mass measurement could, in the most favorable instances, produce an isomer-specific structure postulation. Where the technique was successful, it was outstandingly successful. However, the technique at the Research Triangle Institute is still experimental and the success rate was not as high as desired for a variety of reasons. With some method development and experience in the use of the technique, the Fourier transform infrared technique will prove to be an invaluable adjunct to the mass spectrometric techniques already available. The chief drawback to full utilization of infrared techniques lies in the area of sensitivity: the sample requirements for successful use of infrared can often not be met by environmental samples.

5) laboratory cleanup procedures. The laboratory cleanup procedures proved outstandingly successful in the attainment of their objective: the separation of polar from nonpolar (mainly hydrocarbon) constituents. As a general rule, the samples which had been put through the cleanup process exhibited polar components which either had not been observed or which had been very difficult to observe above the high background of hydrocarbon consitutents. The extract cleanup

was successful and would be a major aid in the characterization of an extract in enabling components to be seen which would not otherwise be observed or identifiable. If the objective were to deconvolute the hydrocarbons, still further laboratory procedures would be called for. It is also possible, in the course of the laboratory cleanup procedure, to separate polynuclear aromatic hydrocarbons from alkane and alkene hydrocarbons. The primary goal of the laboratory cleanup process as used in this program would have been to enhance the probability of successful Fourier transform infrared analysis, had the overall success rate of the Fourier transform infrared analysis been higher.

Most of the analytical methods employed in this program have been found to be very labor-intensive, and labor intensive in the area of highly trained technical personnel. Other than the laboratory cleanup procedures, most of the analytical operations require the commitment of major amounts of time by senior experienced personnel. The capillary gas chromatography/low resolution mass spectrometry procedure used to locate the component of interest requires experienced personnel for most effective utilization because the decisions to be made about correspondence of spectra between the mass spectrum supplied by the Environmental Protection Agency are crucial to the entire subsequent program. Appropriate use of computerized background subtraction techniques and other techniques of mass spectral manipulation are called for, and this level of operation requires highly trained and experienced personnel. Use of capillary gas chromatography with accurate mass measurement is also a technique which requires application of training and extensive experience. The coupled technique is not entirely routine and, without the commitment of highly trained personnel, major amounts of time can be wasted collecting data which are ultimately worthless. Capillary gas chromatography coupled with Fourier transform infrared spectrometry is still an experimental technique, not in routine use in most of the laboratories in this country. The requirement for highly trained (and, therefore, expensive) personnel is obvious. Use of chemical ionization mass spectrometry and interpretation of the results of a given experiment can be difficult even for the most respected and senior professionals in the field. Integration of all the pieces of information which can be generated in the course of use of all the types of analytical procedures available also requires extensive time commitment by a professional analytical chemist. Standards corresponding to most of the postulated structures are almost invariably not available from commercial sources and custom synthesis is expensive from the aspect of commitment of senior professional time in designing the synthesis and trained professional staff in the execution of the synthesis. It would be unusual for a custom synthesis of any minor degree of difficulty to cost less than $1500-2000.

Thus, if the objective of the analytical procedures is to confirm a structural postulation by co-injection of a standard, the following conditions must be met:

1) abundant quantities of sample material must be available since the analytical methods which can provide the most definitive structural information are quite profligate in their use of sample material;
2) extensive resources must be available from the point of view of accessibility to major analytical instrumentation;
3) extensive financial resources must be available in order to make the most effective utilization of analytical techniques which require the use of major instrumentation. Very few people are sufficiently specialized in the wide range of analytical techniques which must be used to avoid intervention of a specialist trained and experienced in the technique to reap maximum benefit from its use;
4) a major financial commitment could be required in order to obtain analytical standards which correspond to the structures postulated. Where there is no possible way to make a decision between two or three possible isomers on the basis of available spectral information, extensive custom synthesis could be required.
5) an overall success rate is very likely to be low in spite of effective utilization of all available techniques. It would be possible, for example, to have several viable possibilities after accurate mass measurement, use infrared spectrometric techniques to pinpoint a

number of functional groups, and still be unable to postulate a definitive structure for a component of interest.

In examining the data obtained from the several types of mass spectrometric analysis employed, one conclusion is obvious. The most efficient and cost-effective way to take advantage of these techniques is to have direct access to a single mass spectrometer where the original capillary gas chromatography/low resolution electron ionization mass spectrometry analysis can be performed. This analysis would then logically be followed immediately by re-injection of the sample and performance of the accurate mass determination. With immediate analysis of the data by the Project Director a decision can be made very quickly whether or not the use of chemical ionization techniques is required, and the appropriate analysis (or analyses) can be performed within a few hours. This mode of operation would allow the Project Director to integrate all of the forms of mass spectral information before making a decision about subsequent analytical procedures. The mode of operation employed in the program was far less than optimal because of a lack of sufficiently flexible instrumentation in the Mass Spectrometry Laboratory of the Research Triangle Institute. There was thus a substantial time lag between, for example, the initial capillary gas chromatography/low resolution mass spectrometry analysis and the accurate mass determination. After both of these forms of information were in hand, a decision was made whether or not to use chemical ionization techniques. The time lag could range from days to weeks to months. With the appropriate instrument readily accessible, all of the information could be obtained, analyzed, and integrated within a matter of hours.

A goal of confirming identification by co-injection of a standard seems to be unrealistic when large numbers of unknowns are involved. None of the compounds for which tentative structures were postulated were commercially available. Some which might logically be available from sources in industry could not be obtained because of company policies. Thus, ultimately, attainment of the goal of confirmation of identification by co-injection of a standard would have required a custom synthesis for each compound. Custom syntheses vary in cost as a function of the difficulty of the synthesis as well as the difficulty of purification and isomer speciation for the product of the synthesis and, in dollar amounts, would probably range upward from a minimum of $1000 per compound. A scheme of custom syntheses on a large scale rapidly becomes financially prohibitive and, depending on priorities, could also become prohibitive in terms of time. In order to use co-injection as a confirmation technique, priorities would have to be evaluated very carefully and, for fifty components of interest, perhaps a rate of no more than 10% custom syntheses would be realistic. For the project, the complete lack of commercial availability of even related compounds was not anticipated.

Repeated observation of the concentration level of components of interest indicates that levels as high as one hundred micrograms of material in an entire extract are rare. The final extract volume was 1 mL, which was diluted to 5 mL for storage and shipping. The original volume of water would have to be increased significantly in order to obtain higher levels of analyte. In the context of the present program, this was not possible. Therefore, nuclear magnetic resonance spectroscopy, which would have been a truly definitive tool in assigning structures, was inaccessible because sample requirements for application of the technique are too high. Unless the overall sample taking/sample processing/sample purification steps can be adjusted to the sample size requirement of nuclear magnetic resonance spectroscopy, application of this technique is simply not feasible and it should not even be considered as a possibility.

Some of the same restrictions apply to the coupled capillary gas chromatography/Fourier transform infrared (FT-IR) spectrometry technique, even when using the Unacon automatic concentrator interfaced to the capillary gas chromatograph. FT-IR sample requirements can be one or two orders of magnitude higher than mass spectrometric sample requirements, and major improvements in that level of sensitivity await technological advances in several areas. However, the application of the Unacon/capillary gas chromatograph/FT-IR technique would benefit from some extensive exploration and method development here at the Research Triangle Institute. In the present system, the interface between the gas chromatograph and the FT-IR spectrometer is far too unwieldy. Some fairly extensive studies need to be performed to establish the correlation between GC/MS, GC/FT-IR, and GC with flame ionization detection. It should also be possible to optimize gas chromatograph/FTIR spectrometer design parameters to facilitate the combined analysis. One of the most valuable techniques for compound identification in mass spectral analysis is computerized library search. Computerized library search is also extremely valuable in the interpretation of data obtained from the FT-IR. However, libraries presently available are very limited in terms of number of compounds. Extensive libraries of IR data are available, but the extensive libraries do not have the compounds in the vapor phase and there are substantial differences in the IR spectra obtained in condensed phase vs. vapor phase. Accumulation of much more data in gas phase IR libraries is obviously a very desirable goal, but one which will require painstaking analysis and documentation of spectral quality. The ideal method of operation using the mass spectrometer and the FT-IR would be a coupled analysis which combines the two techniques. The power of a combined extract concentrator/capillary gas chromatograph/FT-IR/MS (or even FT-IR/MS/MS) in determining compound structure, especially with speciation of functional groups as provided by the FT-IR, would provide a tremendous advantage to the investigator with a mandate to determine the structure of a complete unknown which is present in a relatively complex mixture.

A further recommendation can be made with regard to the application of chemical ionization techniques. As discussed previously, these techniques have their greatest value when they can be applied in close temporal proximity to other forms of mass spectral analysis. Since the exact nature of the chemical ionization reactions which occur is often difficult to ascertain when the compound in question is a complete unknown, integration of electron ionization data with the data from one or two or even three forms of chemical ionization would be beneficial. In the ideal case, one observes an ion of mass M in the electron ionization mass spectrum and this ion is observed at mass $(M+1)^+$ in the chemical ionization mass spectrum, with the two analyses being performed back-to-back in order to be certain that the same compound is being analyzed in both cases. However, depending upon the identity of the compound of interest, chemical ionization techniques can produce ions by charge exchange, by protonation, by formation of an $(M-X)^+$ species, by an addition/cleavage reaction, and especially for the hydrocarbon reagent gases, by addition of various alkyl groups. A priori, especially when the compound is a complete unknown, it is impossible to predict exactly what chemistry will occur, and interpretation of data obtained by chemical ionization may not be straightforward. Use of chemical ionization techniques realizes its optimum potential as part of an integrated scheme of analysis where a sequence might be, for example, initial analysis of Extract X by capillary gas chromatography/ low resolution electron ionization mass spectrometry to establish the presence of the component of interest. This analysis would be followed immediately by capillary gas chromatography/accurate mass measurement, to determine an elemental composition for the component of interest (or to obtain a listing of the possibilities if these possibilities cannot be narrowed down to a single choice at this point). The next analysis might possibly incorporate methane chemical ionization, using accurate mass measurement techniques, with subsequent isobutane and/or ammonia chemical ionization again coupled with accurate mass measurement. Concatenation of this type of information would be invaluable, in many cases, in determining a molecular weight for the component of interest. It may very well require the integration of several forms of chemical ionization/accurate mass measurement information in order to be able to postulate a molecular weight and an elemental composition with any degree of certainty. In many cases, even with availability of all these forms of information, it may be impossible to confine the possibilities to a single choice or, indeed, to feel confident of having accurate molecular weight information at all.

One type of compound which is of major interest in the environmental area is halogenated alkanes, alkenes, and cyclic compounds. Confident identification of these types of compounds encounters many difficulties. A major difficulty is the nature of the mass spectra obtained under electron ionization conditions. These compounds do not produce molecular ions. They fragment extensively and the ions observed are very frequently not even remotely characteristic of the molecular weight of the compound or of the number of halogen atoms contained in the molecule. Mass spectral data compendia offer very little assistance in the interpretation of the mass spectra of these types of compounds. Beyond extensively chlorinated three-carbon alkanes, the number of standard spectra for alkanes containing two or more chlorine atoms is very small. This problem is primarily due to the lack of availability of isomerically pure standards which can be analyzed so that the mass spectra can be entered into the compendia and libraries. When chemical ionization techniques (either the positive or negative mode) are employed in an effort to obtain molecular weight information, results are discouraging. In the mass spectrometric literature, no technique has so far been reported which will reliably yield molecular weight information for these types of compounds under any presently known conditions. If the importance of these types of compounds is great enough, efforts should be made in several areas: 1) standards should be synthesized so that electron ionization mass spectra can be obtained and included in the compendia and libraries in most common use; 2) with the availability of standards, relative retention data can be established to aid in compound identification; 3) research in the area of chemical ionization techniques may yield some techniques for producing molecular weight information for these types of compounds.

During this program, further efforts beyond the initial capillary gas chromatography/electron ionization low resolution mass spectrometric assay were made only in the event that the compound of interest was observed and still could not be identified. Where the compound could not be observed or a good identification could be made on the basis of the mass spectrum deconvoluted by capillary resolution with subsequent computerized library search, no further effort was made. A few representative examples will be discussed in some detail. The rest of the extracts which were not the subjects of extended analytical efforts are summarized in Table 5.1, with the mass spectra for the compounds of interest presented in Appendix A.

Table 5.1. Summary of Data for Extracts Not Analyzed Further

Run Number	Type	Industry	Treatment Stage	Frequency of Occurrence*	Disposition
663	Acid	Pharmaceuticals	Pharm., Influent	12	Spectrum only similar.
958	B/N	Paint and Ink	N/A	18	No similar spectrum found.
961	B/N	Paint and Ink	N/A	16	Matching spectrum at scan #2537; no good library identification. Tentative manual identification as a siloxane; no further interest.
1135	Acid	Pulp and Paper	SDWP02(R) Influent Pulp Mill	N/A	Matching spectrum found at scan #3007; identified by the library as 4-hydroxy-3-methoxybenzaldehyde (vanillin) with a FIT of 994; why was the original computer indentification not made?
				N/A	Matching spectrum found at scan #4505; identified by the library as 1-(4-hydroxy-3,5-dimethoxyphenyl)-ethanone (acetosyringone) with a FIT of 993; why was the original computerized identification not made?
1222	B/N	Rum	SE-001A(C)	6	Spectrum only similar.
1235	B/N	Rum	SC-001A(E) Final Stop	15, 16	Spectra not found.
1630	B/N	Publicly Owned Treatment Works	Refinery Effluent	5	Spectrum not found.
1691	Acid	Publicly Owned Treatment Works	Refinery B	5	Spectrum not found.
1699	B/N	Publicly Owned Treatment Works	Refinery C	5	Spectrum not found.
1733	B/N	Leather Tanning	Process Grab	N/A	Spectrum only similar.
2373	Acid	Inorganic Chemicals	Effluent Pond	21, 10	One spectrum appeared to be a tetrachlorophenol but was not observed in the extract; other spectrum not found.
2965	Acid	Publicly Owned Treatment Works	Refinery F	5	Spectrum appears to be a mixture of components; exact match not found.
2981	B/N	Pulp and Paper	Treated Effluent	N/A	Spectrum only similar.
4050	Acid	Pulp and Paper	Composite	6, 6	Spectra only similar.
4064	Acid	Pulp and Paper	Mixing Chamber	9	Matching spectrum at scan #2495; library identification of 3,4-dimethylphenol with FIT of 930; why was computer identification not made originally?

(continued)

Table 5.1 (continued)

Run Number	Type	Industry	Treatment Stage	Frequency of Occurrence	Disposition
4139	B/N	Pesticides Manufacturing	Nonvolatile Organics	5	No similar spectrum found.
4748	B/N	Electronics	Influent to Equalization	6,6,5,5,9,22,6,6	Tentative manual identification as caranone; no further interest. Appears to be a hydrocarbon combined with C_6-alkylbenzene; several C_6-alkylbenzenes present; extensive hydrocarbon background. No further interest. Spectrum of a composite of hydrocarbon and saturated and unsaturated C_5-alkylbenzenes; no further interest. Spectrum a composite of saturated and unsaturated C_5- and C_6-alkylbenzenes; no further interest. No similar spectrum found. Spectrum tentatively identified as methylbiphenyl isomer; similar spectra found; no further interest. No similar spectrum found - possibly composite deconvoluted by capillary resolution.
5152	B/N	Mechanical Products	Kolene Air Scrubber	15	Only similar spectra found.
5205	B/N	Coal Mining	Untreated Effluent Slurry	15	Only similar spectra found.
5207	B/N	Coal Mining	Untreated Effluent Slurry	17	Only similar spectra found.
5425	Acid	Mechanical Products	Paint and Booth Water Curtain	35, 22	No similar spectrum found.
5671	Acid	Printing and Publishing	WT-006 Effluent Grab	15	Determined to be a hydrocarbon ($C_{13}H_{28}$) upon accurate mass measurement; no further interest.
5969	B/N	Publicly Owned	Influent Composite	47	Spectrum not found.
7979	B/N	Petroleum Refining	N/A	5	Spectrum appears to be a composite. No similar spectrum found possibly because of capillary resolution.
8218	Acid	Timber Products	Celotex Raw Waste	9	Only similar spectrum found.
8283	B/N	Timber Products	Kerr McGee Raw Waste	N/A	Spectrum found, identified as a cresol isomer; why was computer identification not made originally?

(continued)

Table 5.1 (continued)

Run Number	Type	Industry	Treatment Stage	Frequency of Occurrence	Disposition
8320	B/N	Timber Products	Prim. Penta Oil-H20 Grav Sep at 311 Weir	58	No similar spectrum found.
8751	B/N	Ore Mining	Plant Intake	5	No similar spectrum found.
8789	Acid	Ore Mining	East Pond Effluent	N/A	Spectrum looks like a dichlorobenzoic acid but not identified by computer; similar spectrum not found.
8996	Acid	Publicly Owned Treatment Works	Untreated Effluent	37	No similar spectrum found.
9275	B/N	Mechanical Products	Centrifuge Effluent	6	Spectrum appears to be a C_4-alkylbenzene with some extraneous ions; at least ten C_4-alkylbenzene isomers are present in the extract.
9284	B/N	Mechanical Products	Centrifuge Effluent	10	No similar spectrum found.
9381	B/N	Soaps and Detergents	N/A	50	No similar spectrum found.
9914	B/N	Inorganic Chemicals	Treated Effluent	12	No similar spectrum found.
12109	B/N	Organics and Plastics	N/A	N/A	Extract examined for the presence of chlorinated compounds: dichloro- and trichlorobenzenes found, chloroaniline also found. No chloronitrobenzenes found.
13158	B/N	Publicly Owned Treatment Works	Influent	N/A	No similar spectrum found.
13614	Acid	Iron and Steel Manufacturing	Untreated Effluent	14	No similar spectrum found.
13738	B/N	Publicly Owned Treatment Works	Untreated Chlorinated Influent	16	Matching spectra found at scans #1574, 1612, 1729; identified by the library as dimethoxyphenol isomers; no further interest. Why was an original computerized identification not made?
14615	B/N	Organic Chemicals	Disch. 002 Holding POnd Disch. Thru 002	8	No similar spectrum found.
15850	B/N	Organics and Plastics	Combined Resin & PHA	N/A	No similar spectrum found.
16610	B/N	Synfuels	SP#2 Rectifier Bottoms	30	Upon accurate mass measurement the the compound was identified as $^2H_8$-naphthalene.
17897	B/N	Organics and Plastics	N/A	N/A	No similar spectrum found.
19245	Acid	Electronics	Influent	8, 9	No similar spectra found.

*Frequency of occurrence is determined by the number of identifications of each compund in the 4"00 sample survey. For a compound where the spectrum was not matched in the reference library, frequency of occurrence is determined by the number of times the unknown spectrum matched other unknown spectra that had relative retention times ± 0.1 that of the first unknown.

EXTRACT 1874 (ACID), COAL MINING INDUSTRY, TREATED EFFLUENT

The chromatogram obtained from the packed column analysis of this extract is presented in Figure 5.2. The mass spectrum of the compound of interest sought by the Environmental Protection Agency is shown in Figure 5.3. The capillary chromatogram of this extract is shown in Figure 5.4. The major ions of the mass spectrum were sought by ion chromatography, but (as demonstrated in Figure 5.5) all of the major ions of the mass spectrum could not be found together in a single mass spectrum (the occurrence of four of the ions is observed in the standard, 2-fluorobiphenyl). The conclusion was, therefore, that the compound of interest could not be found in the extract.

EXTRACT 2955 (ACID), PUBLICLY-OWNED TREATMENT WORKS, REFINERY D

The chromatogram obtained from the packed column analysis of this extract is presented in Figure 5.6. The mass spectrum of the compound of interest is shown in Figure 5.7. The capillary chromatogram of this extract is shown in Figure 5.8. An ion chromatogram showing the major ions of the spectrum supplied by the Environmental Protection Agency is shown in Figure 5.9. The ion chromatograms do not show all of the major ions of the mass spectrum of the compound of interest occurring together, with a base peak of mass 168. Several of the mass spectra indicated as similar by the ion chromatograms were plotted (see Figures 5.10-5.14), but an inspection of any of these mass spectra shows that they are, at best, only similar to the mass spectrum of the compound of interest; not one of them is the same. It thus seems probable that the mass spectrum of the "compound" of interest shown in Figure 5.7 is actually a mass spectrum obtained from coeluting compounds which no longer coelute under capillary chromatography conditions. The conclusion was, therefore, that the compound of interest could not be found in the extract.

EXTRACT 8115 (BASE/NEUTRAL), TIMBER PRODUCTS INDUSTRY, EFFLUENT

The chromatogram obtained from the packed column analysis of this extract is presented in Figure 5.15. The mass spectrum of the compound of interest is shown in Figure 5.16. The capillary chromatogram of this extract is shown in Figure 5.17. A mass spectrum similar to the mass spectrum supplied by the Environmental Protection Agency is shown in

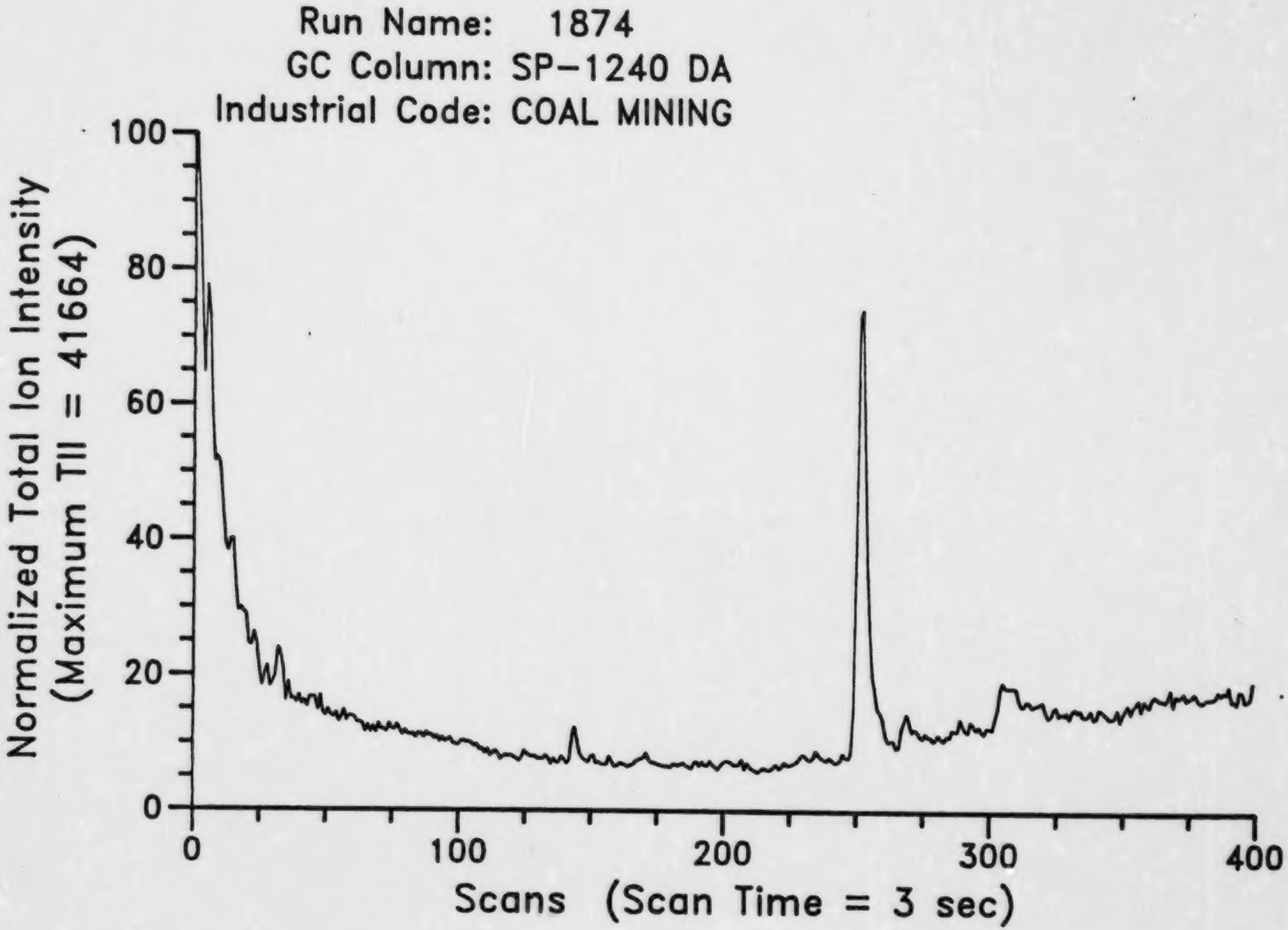


Figure 5.2. Packed column chromatogram of extract 1874 (acid), coal mining industry.

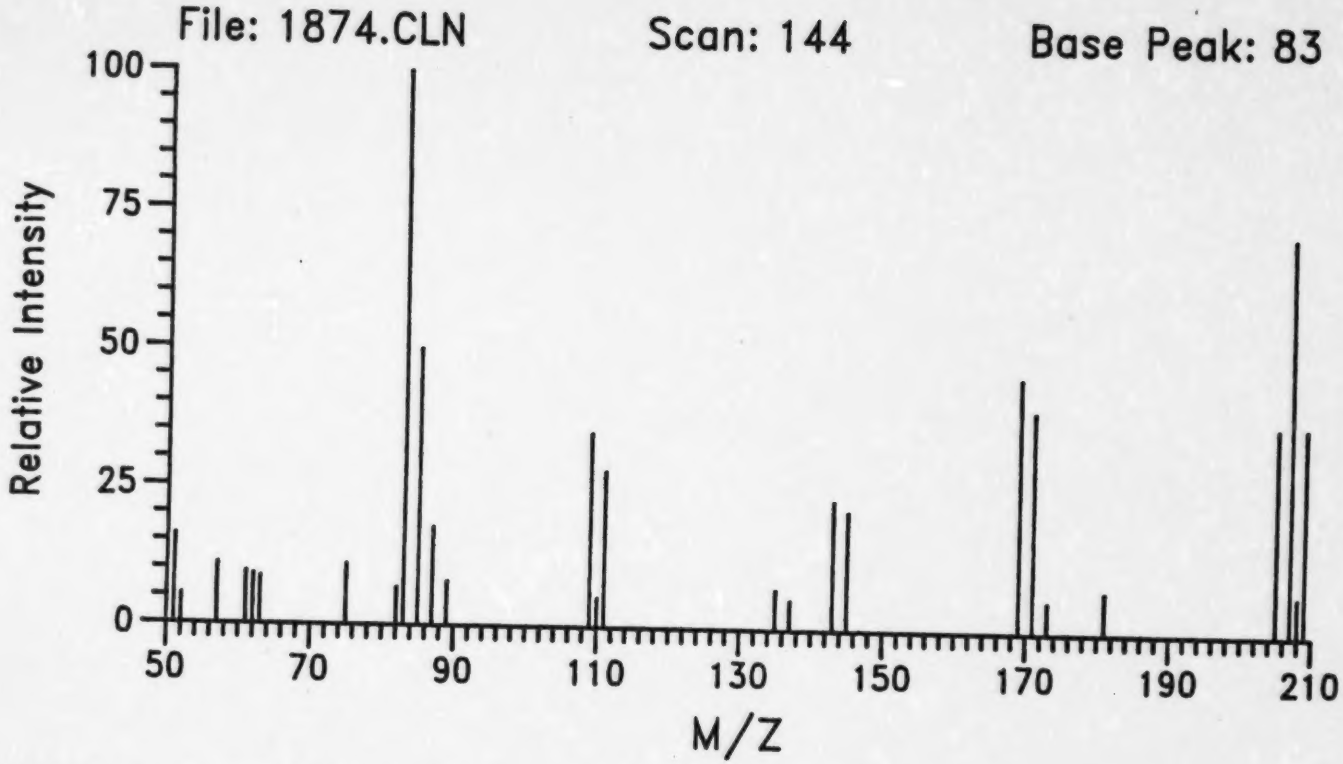


Figure 5.3. Extract 1874 (acid), coal mining industry. Frequency of occurrence: 15.

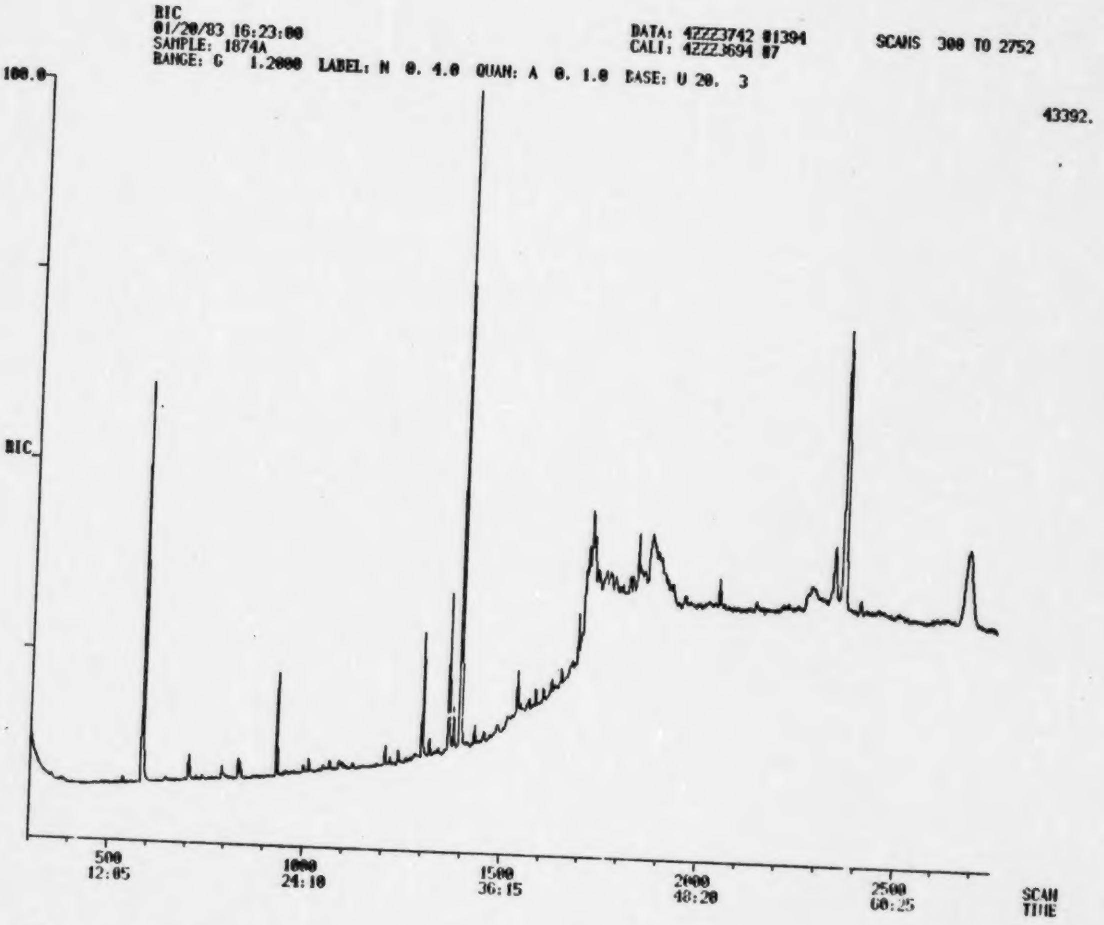


Figure 5. 4. Capillary chromatogram of extract 1874 (acid), coal mining industry.

No similar spectrum found!

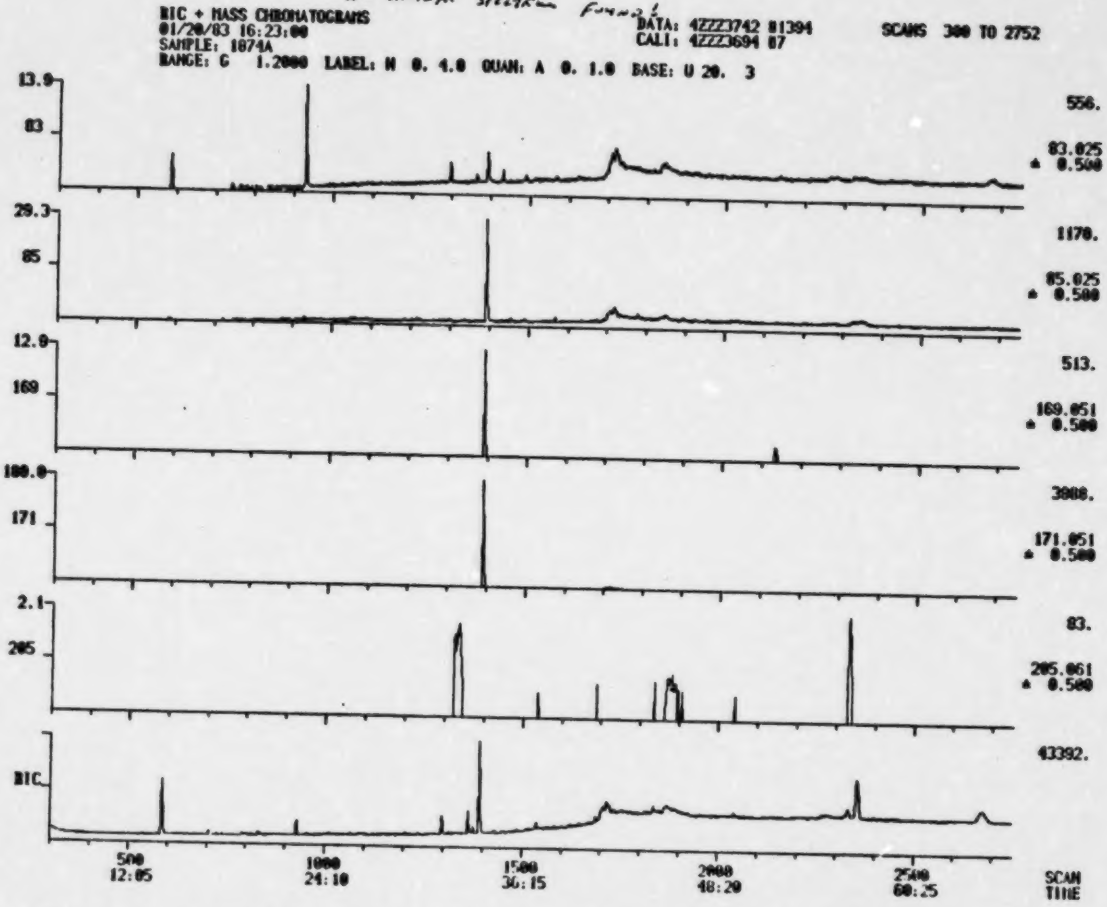


Figure 5.5. Extract 1874 (acid), coal mining industry. Ion chromatogram of m/z 83, 85, 169, 171, 205, which do not occur together.

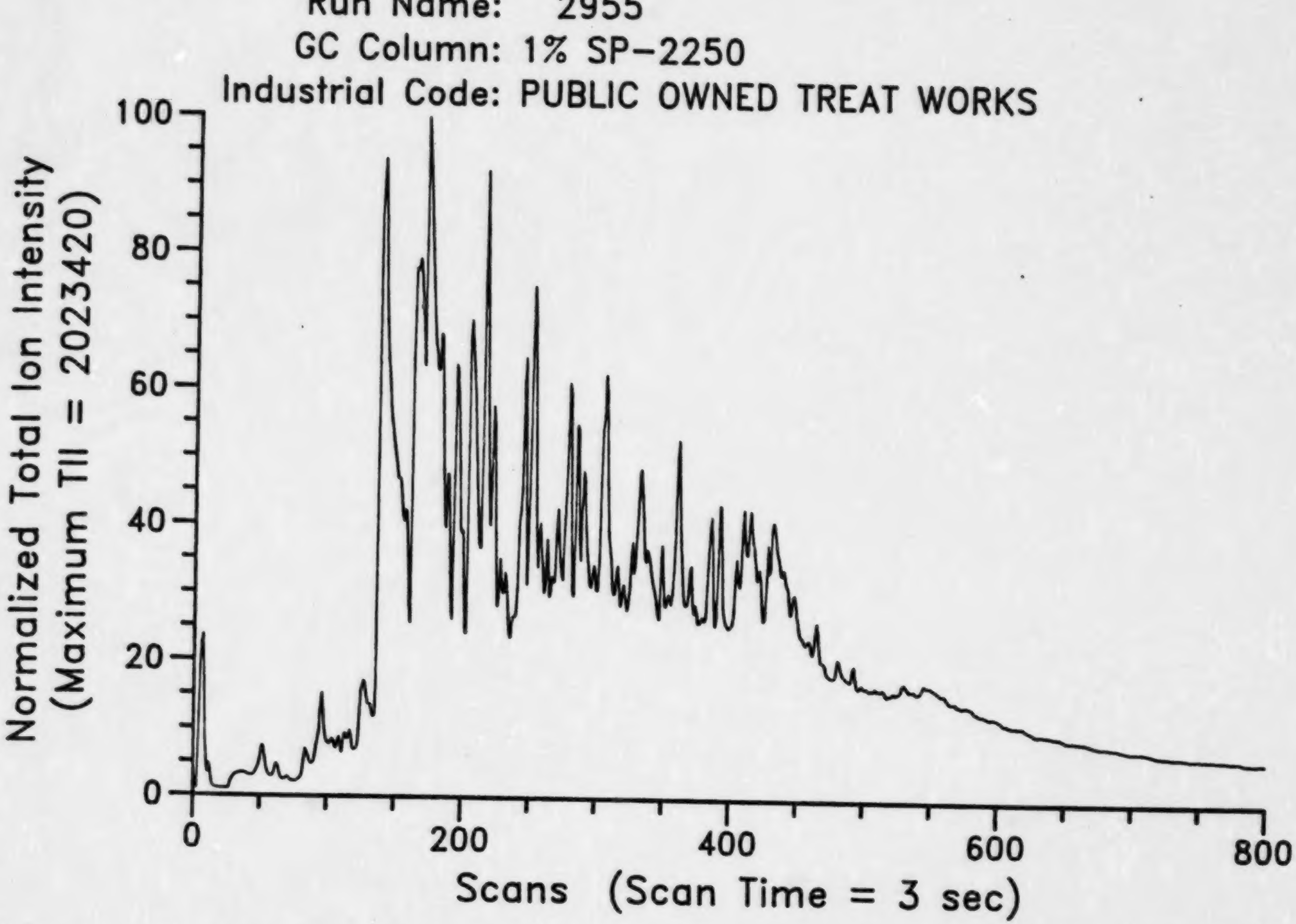


Figure 5.6. Packed column chromatogram of extract 2955 (acid), publicly owned treatment works.

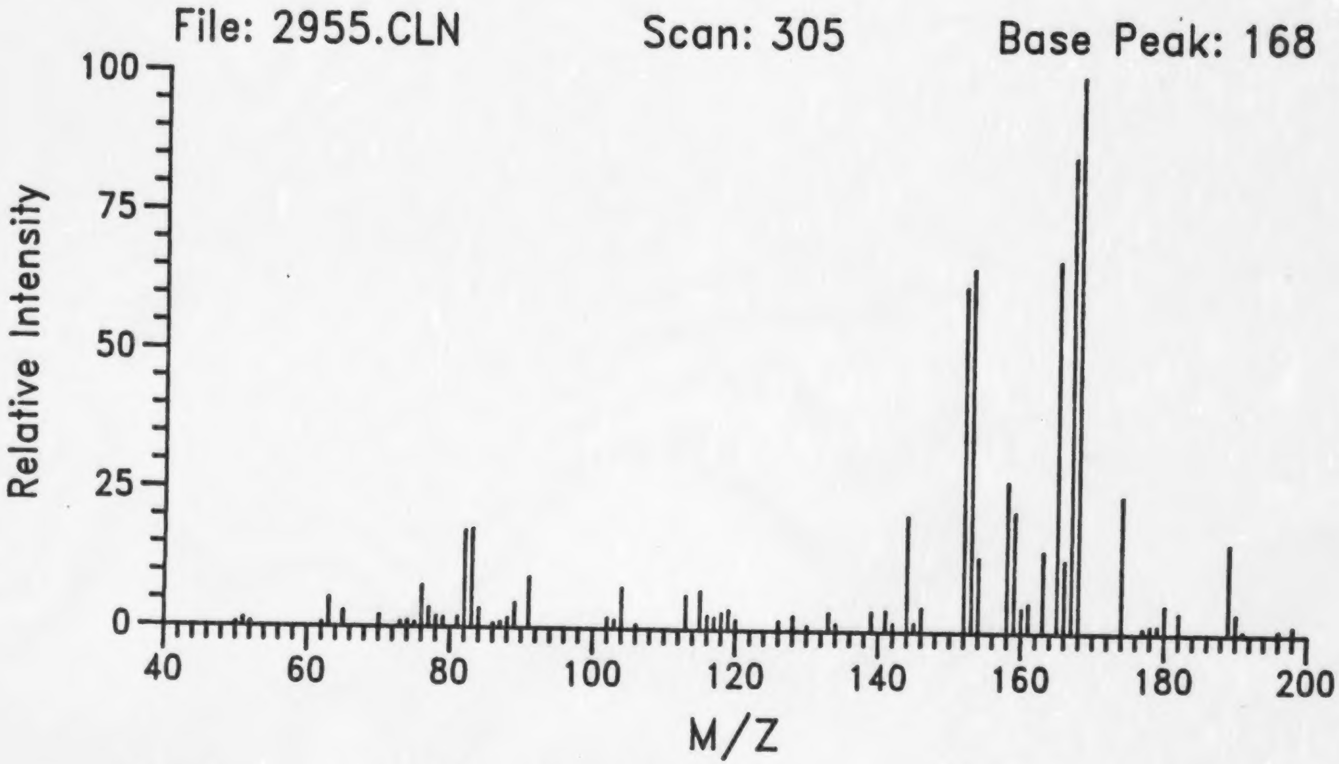


Figure 5.7. Extract 2955 (acid), publicly owned treatment works. Frequency of occurrence: 5.

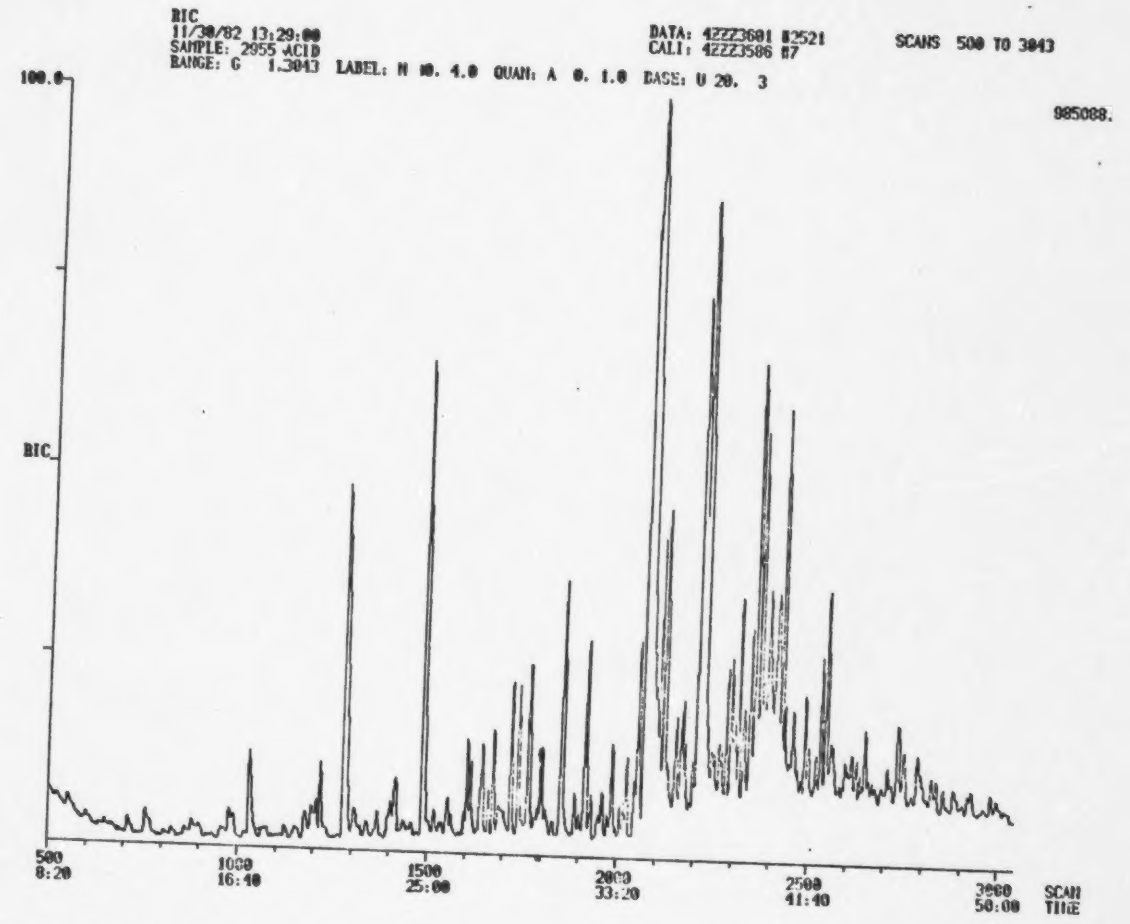


Figure 5.8. Capillary chromatogram of extract 2955 (acid), publicly owned treatment works.

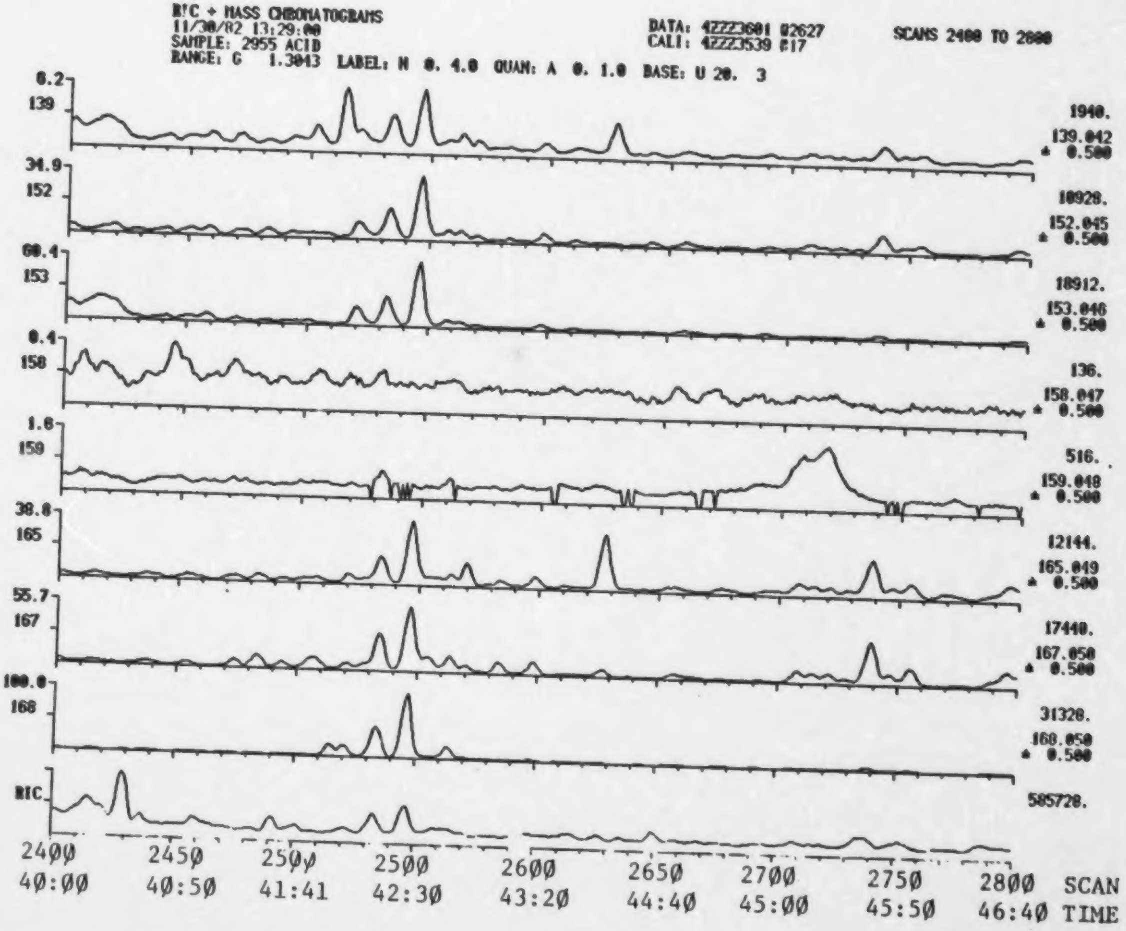


Figure 5.9 Extract 2955 (acid), publicly owned treatment works. Ion chromatogram of m/z 139, 152, 153, 159, 165, 167, and 168.

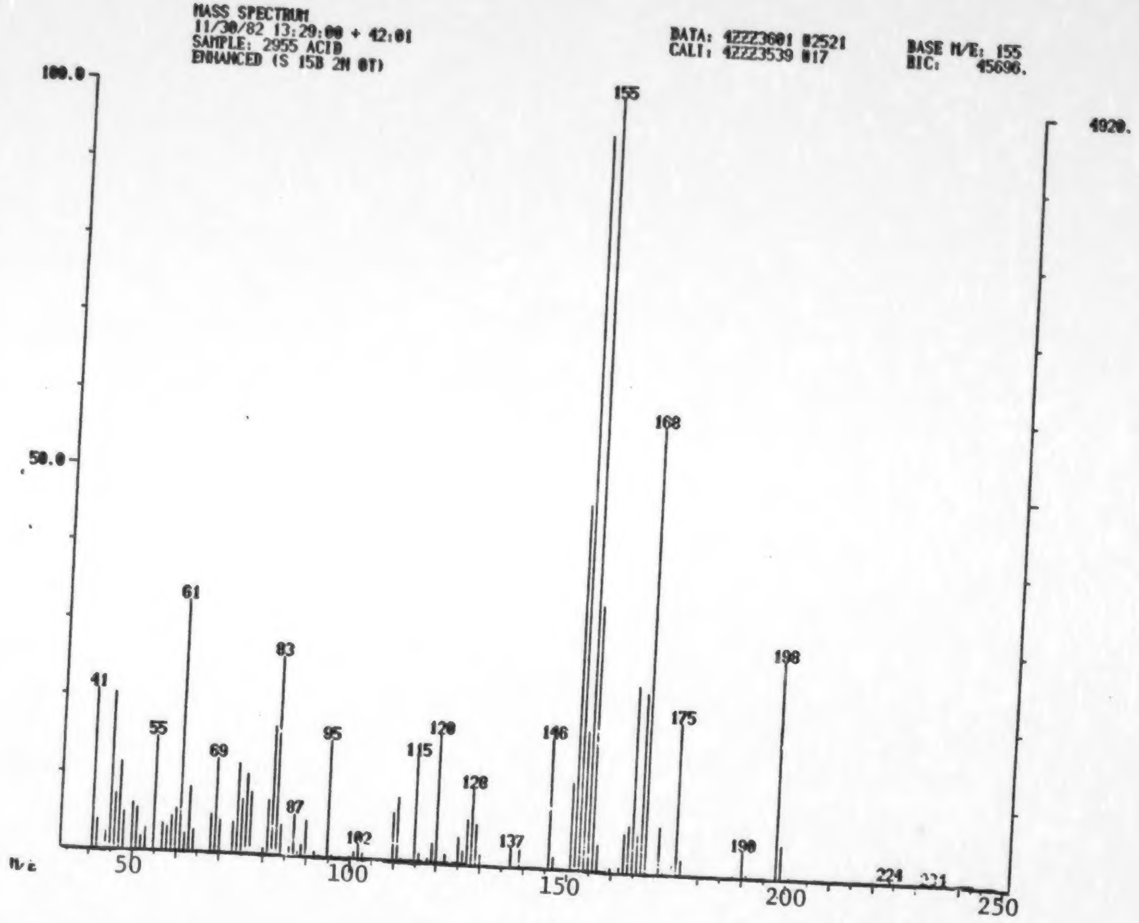


Figure 5.10 Mass spectrum similar to EPA compound of interest.

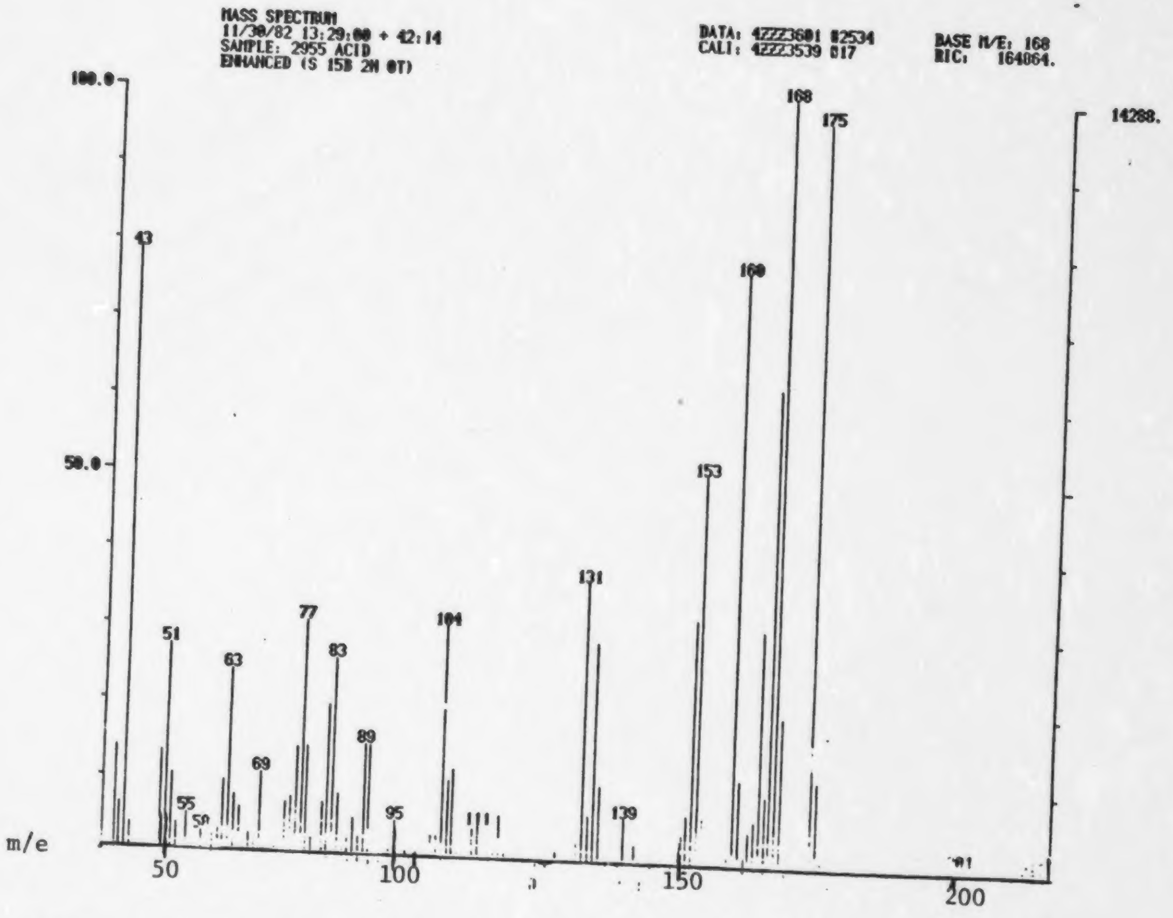


Figure 5.11 Mass spectrum similar to EPA compound of interest.

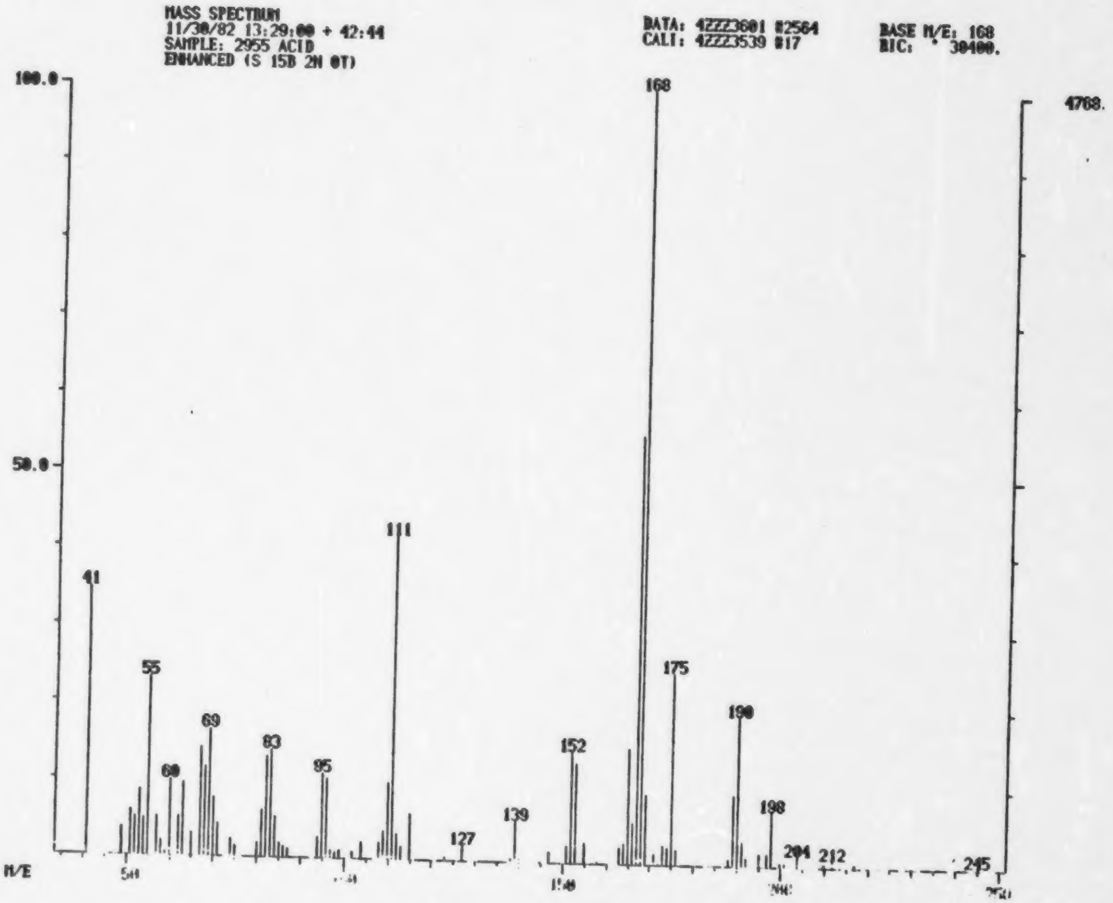


Figure 5.12 Mass spectrum similar to EPA compound of interest.

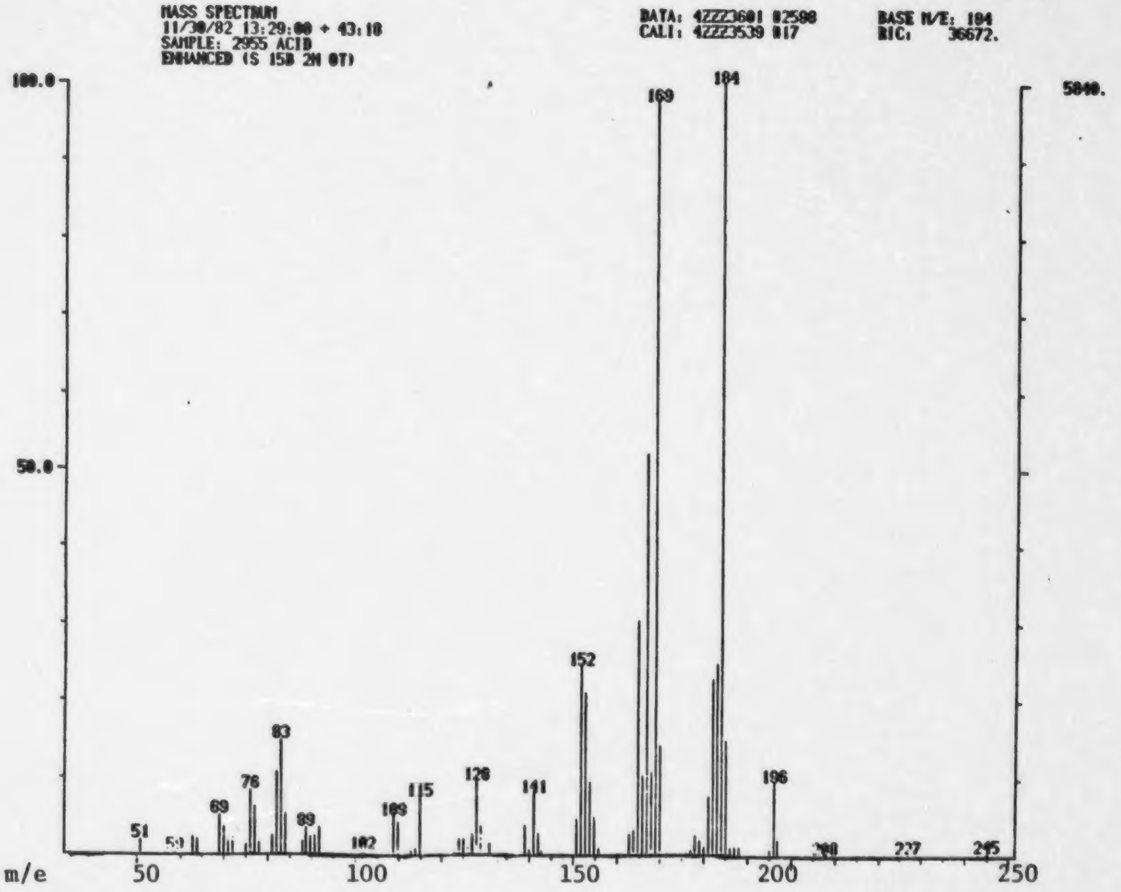


Figure 5.13. Mass spectrum similar to EPA compound of interest.

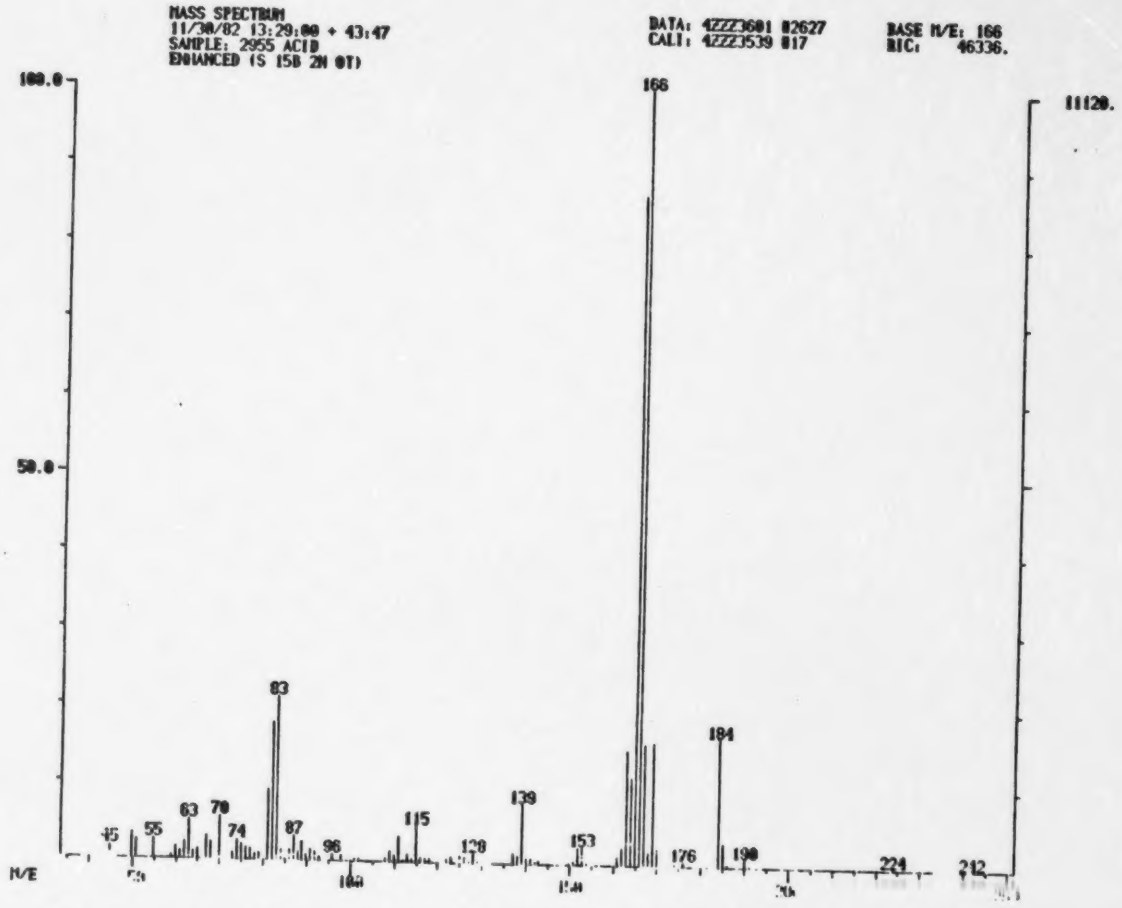


Figure 5.14. Mass spectrum of EPA compound of interest.

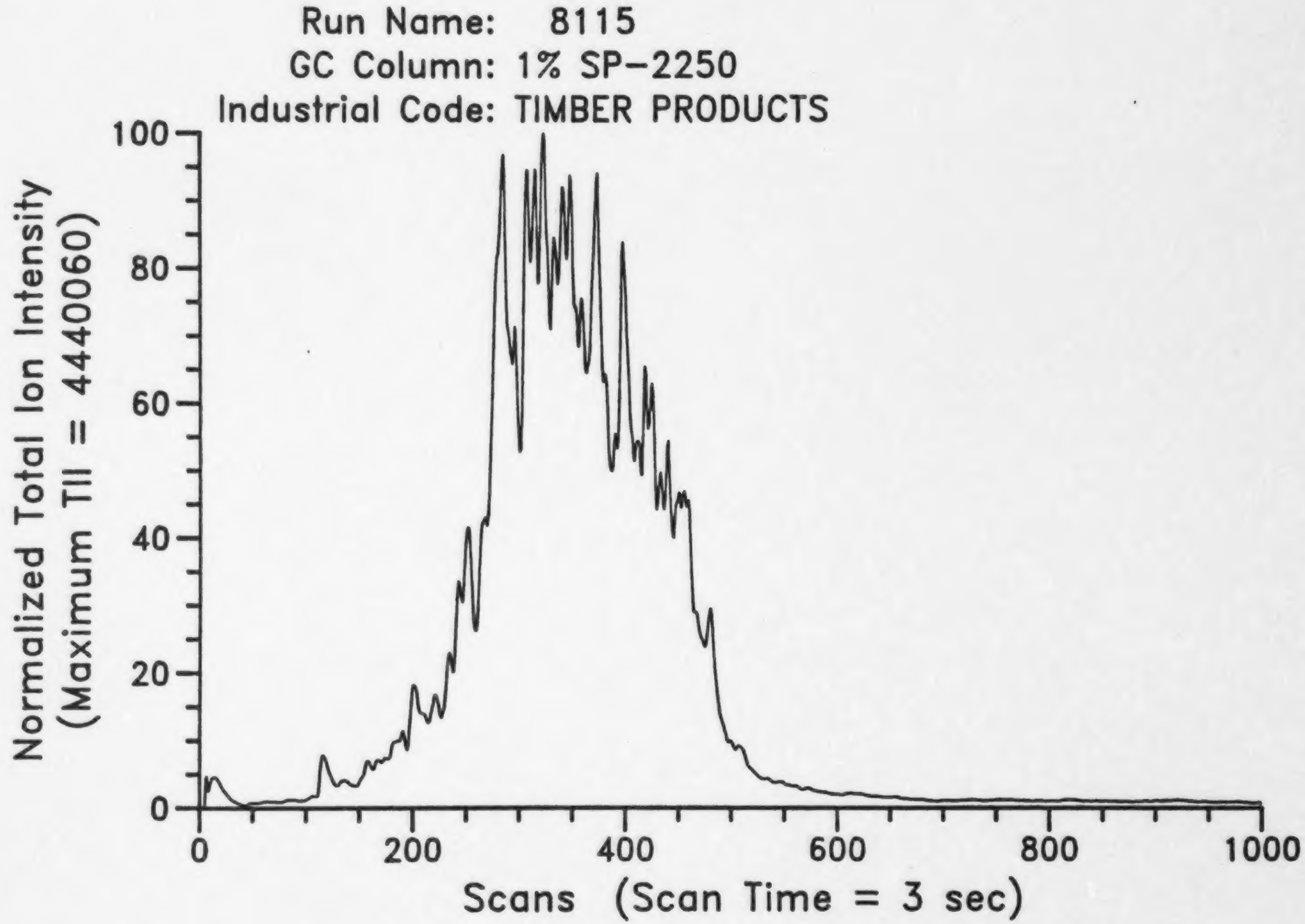


Figure 5. 15. Packed column chromatogram of extract 8115 (base/neutral), timber products industry.

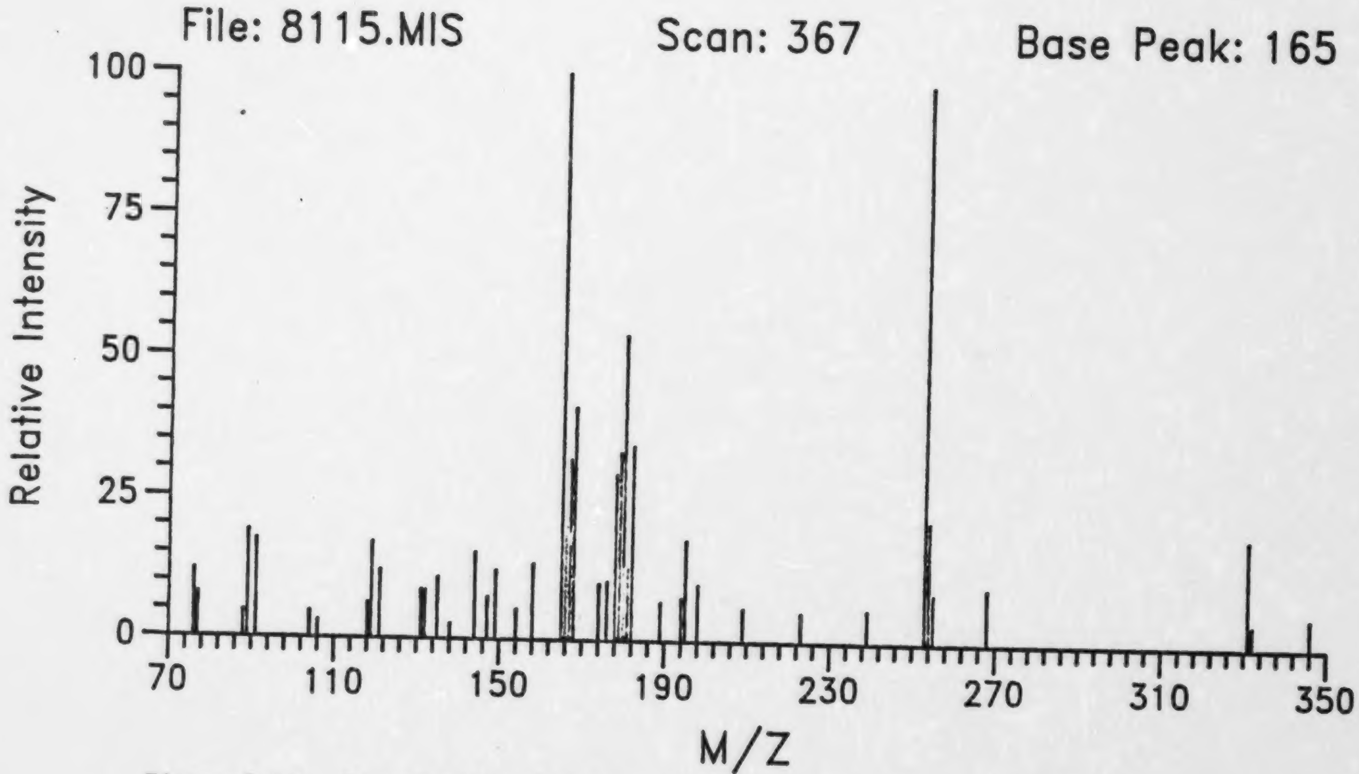


Figure 5.16. Extract 8115 (base/neutral), timber products industry. Frequency of occurrence: 6.

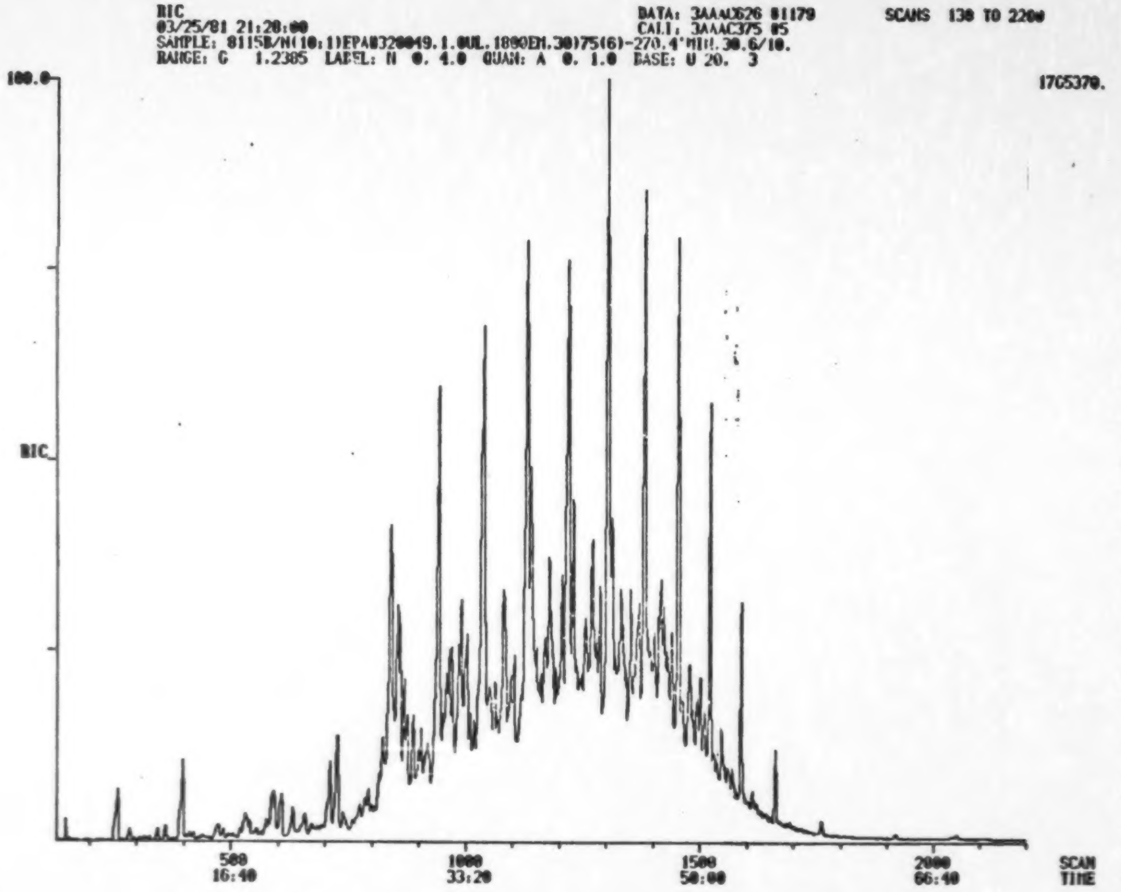


Figure 5.17. Capillary chromatogram of extract 8115 (base/neutral), timber products industry.

Figure 5.18. The computerized library search identifies the mass spectrum as octacosane (Figure 5.19), but the quality of the fit is poor, and a comparison of the mass spectrum of the compound of interest with the top choice selected by the library (Figure 5.20) shows a complete disregard by the library search algorithm of the peaks present at higher masses. The computerized identification is obviously incorrect since no consideration is given to the presence of peaks at m/z 204, 225 and 253. Also, the spectrum obtained from the capillary analysis is, at best, only similar to the mass spectrum supplied by the Environmental Protection Agency--the EPA spectrum shows m/z 165 as base peak, and this peak is not even present in the mass spectrum obtained from the capillary analysis, and the EPA spectrum shows m/z 253 at a relative abundance of approximately 98% vs. approximately 10% for the spectrum obtained from the capillary analysis. A close correspondence between the mass spectrum of the compound of interest and the spectra obtained in the course of the capillary analysis is therefore not attained, and no further analytical work was done on this extract.

EXTRACT 14627 (BASE/NEUTRAL), ORGANIC CHEMICALS INDUSTRY, DOWN DISC. 002 STA. 6

The chromatogram obtained from the packed column analysis of this extract is presented in Figure 5.21. The mass spectrum of the compound of interest is shown in Figure 5.22. The capillary chromatogram of this extract is shown in Figure 5.23. When an ion chromatogram of the major ions of the mass spectrum of the compound of interest is drawn, they all seem to be present at scan #883 (Figure 5.24). However, when the mass spectrum is plotted, and the proportions of the ions are examined (Figure 5.25), no correspondence to the mass spectrum of the compound of interest is obvious. No further analytical efforts were made on this extract.

EXTRACT 20432 (BASE/NEUTRAL), PUBLICLY-OWNED TREATMENT WORKS, TREATED EFFLUENT

The chromatogram obtained from the packed column analysis of this extract is shown in Figure 5.26. The mass spectrum of the compound of interest is presented in Figure 5.27. The capillary chromatogram of this extract is shown in Figure 5.28. An ion chromatogram of the major

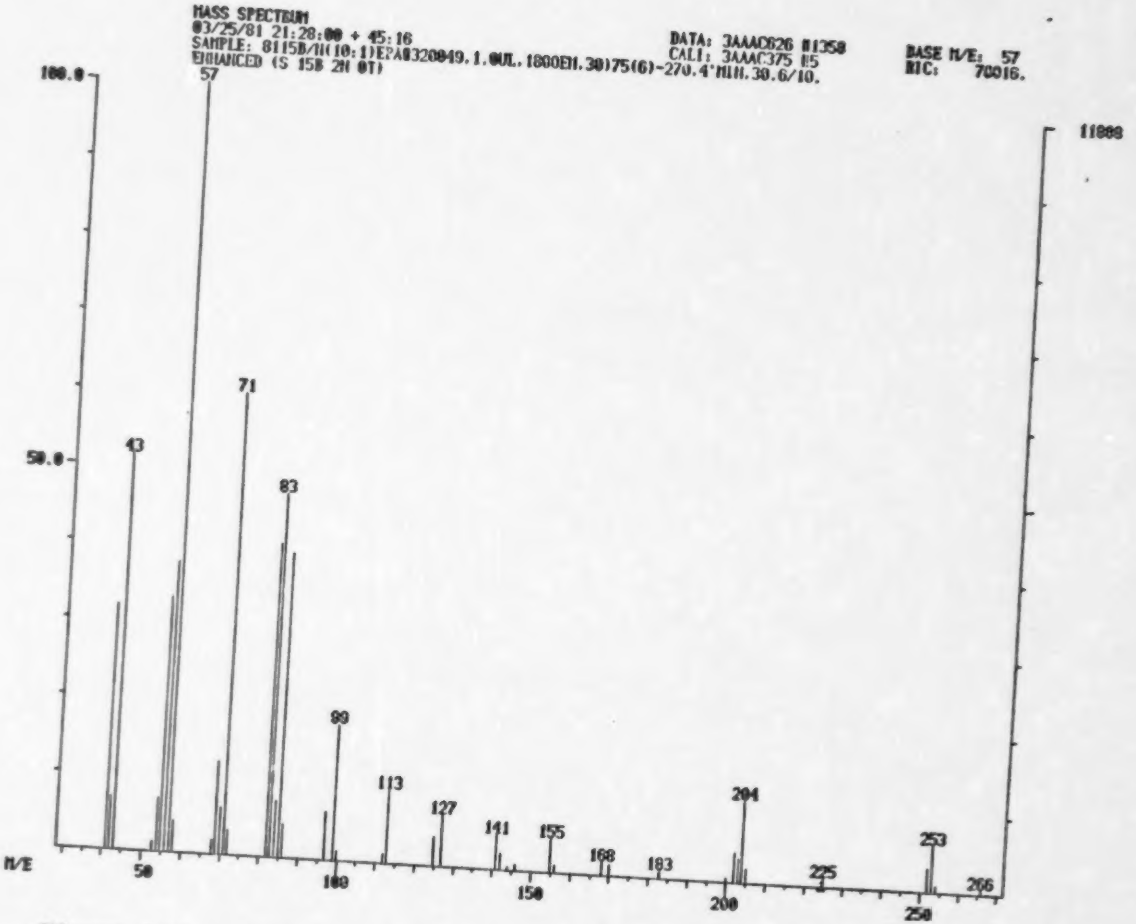


Figure 5.18. Mass spectrum similar to EPA compound of interest.

```
LIBRARY SEARCH                 DATA: 3AAAC626 #1358      BASE M/E:   57
03/25/81 21:28:00 + 45:16      CALI: 3AAAC375 #   5      RIC:     70015.
SAMPLE: 81158/N(10:1)EPA#320049,1.0UL,1800EM,30)75(6)-270,4'MIN,30.6/10.
ENHANCED (S 15B 2N 0T)

25410 SPECTRA IN LIBRARYNB SEARCHED FOR MAXIMUM PURITY
  178 MATCHED AT LEAST 7 OF THE 16 LARGEST PEAKS IN THE UNKNOWN

RANK IN NAME
1  3657 OCTACOSANE
2  3654 DOCOSANE
3  3728 TRICOSANE
4  3147 HEPTACOSANE
5  3660 PENTATRIACONTANE

RANK  FORMULA                         M.WT B.PK   PURITY    FIT   RFIT
1 C28.H58                              394   43      644    869    691
2 C22.H46                              310   43      642    865    685
3 C23.H48                              324   43      635    823    707
4 C27.H56                              380   43      632    853    695
5 C35.H72                              492   57      630    842    699
```

Figure 5.19. Computerized library search of mass spectrum of the compound of interest.

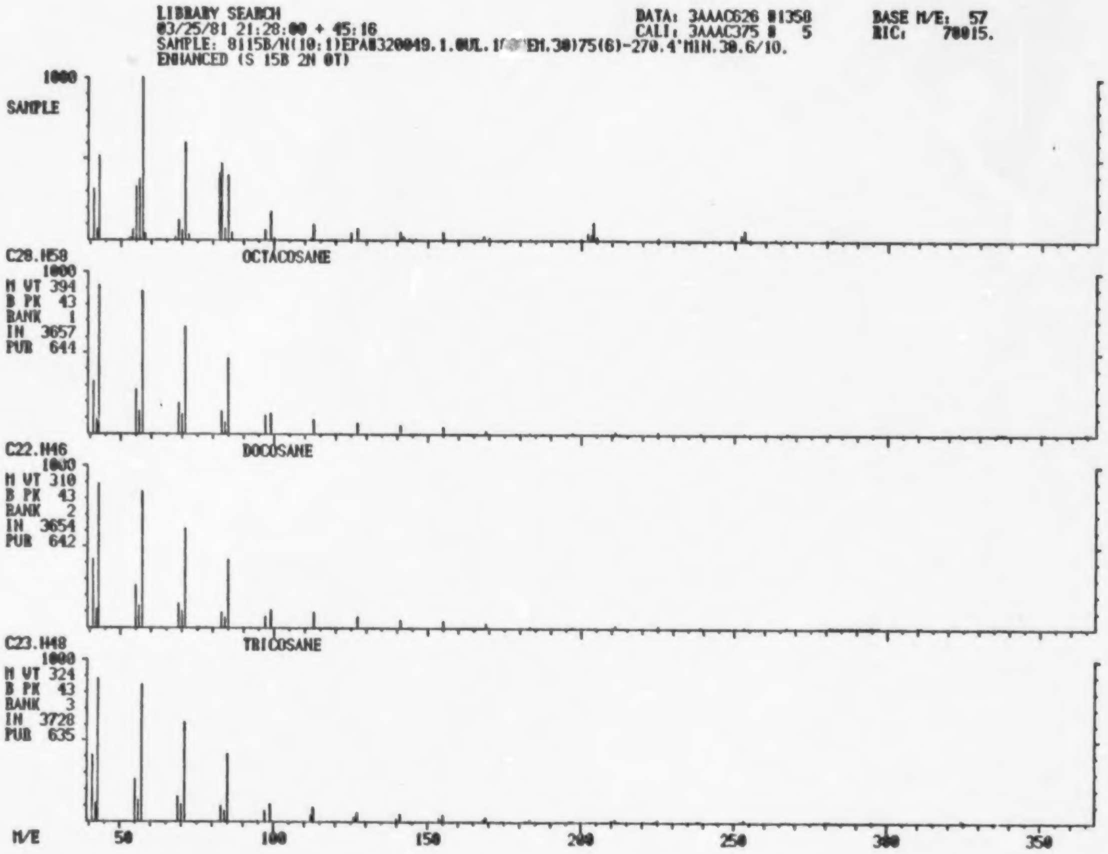


Figure 5.20. Comparison of the mass spectrum of the unknown with choices selected by computerized library search.

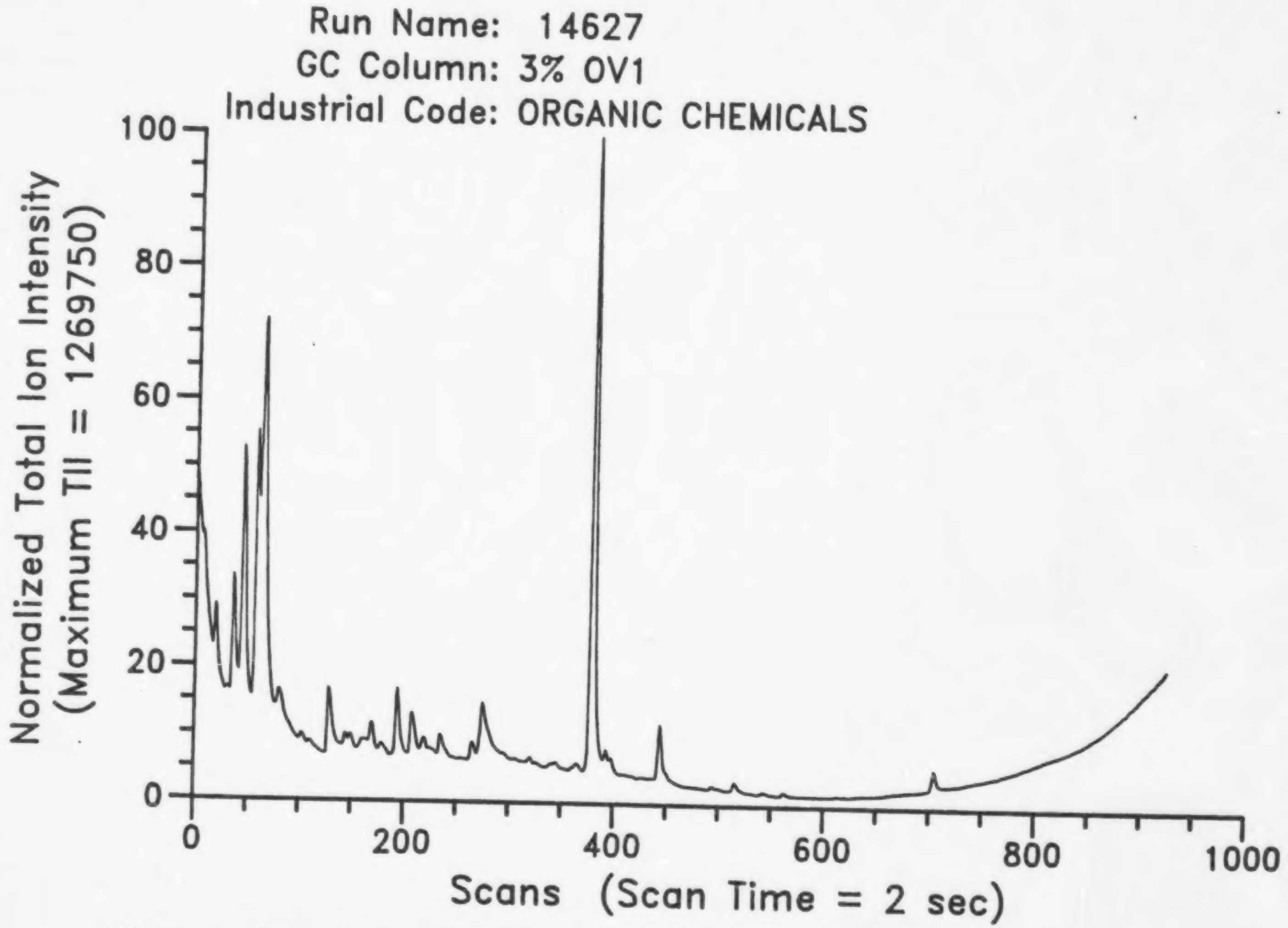


Figure 5.21. Packed column chromatogram of extract 14627 (base/neutral), organic chemicals industry.

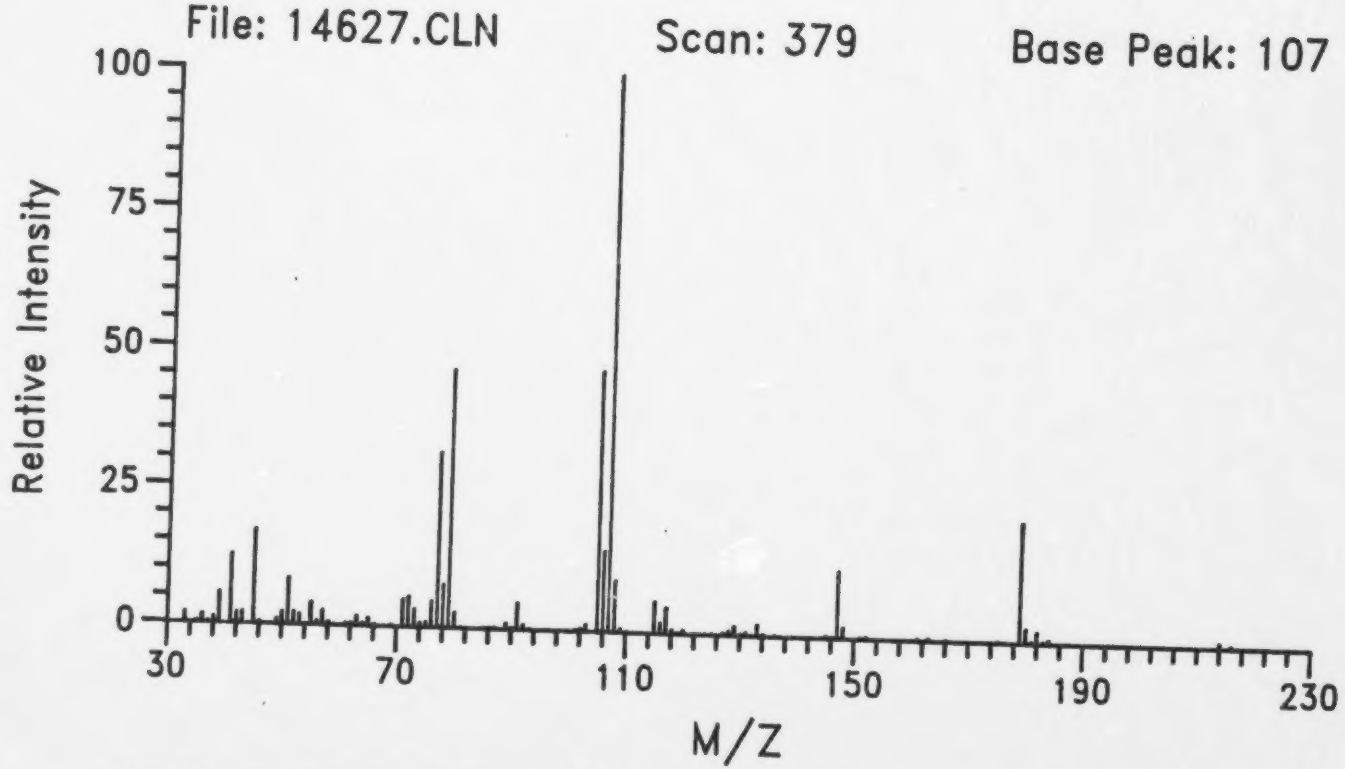


Figure 5. 22. Extract 14627 (base/neutral), organic chemicals industry. Frequency of occurrence: 17

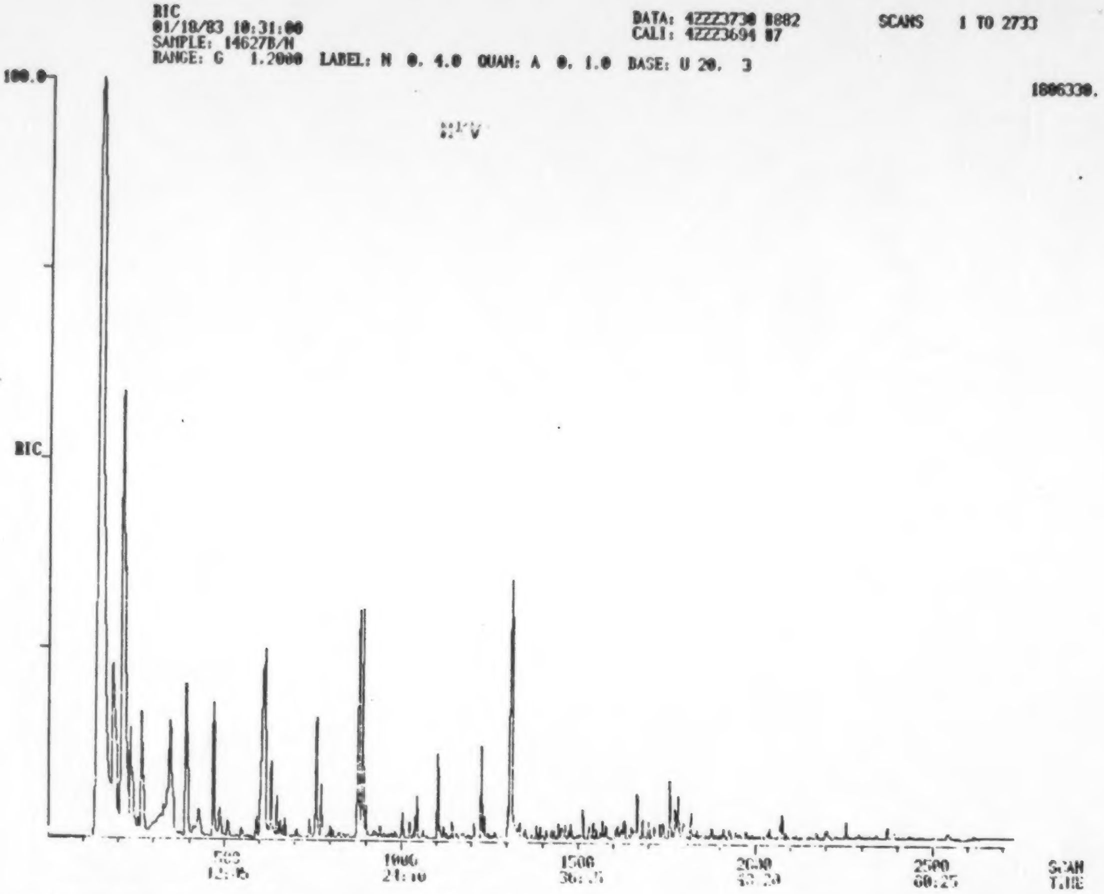


Figure 5.23. Capillary chromatogram of extract 14627 (base/neutral), organic chemicals industry.

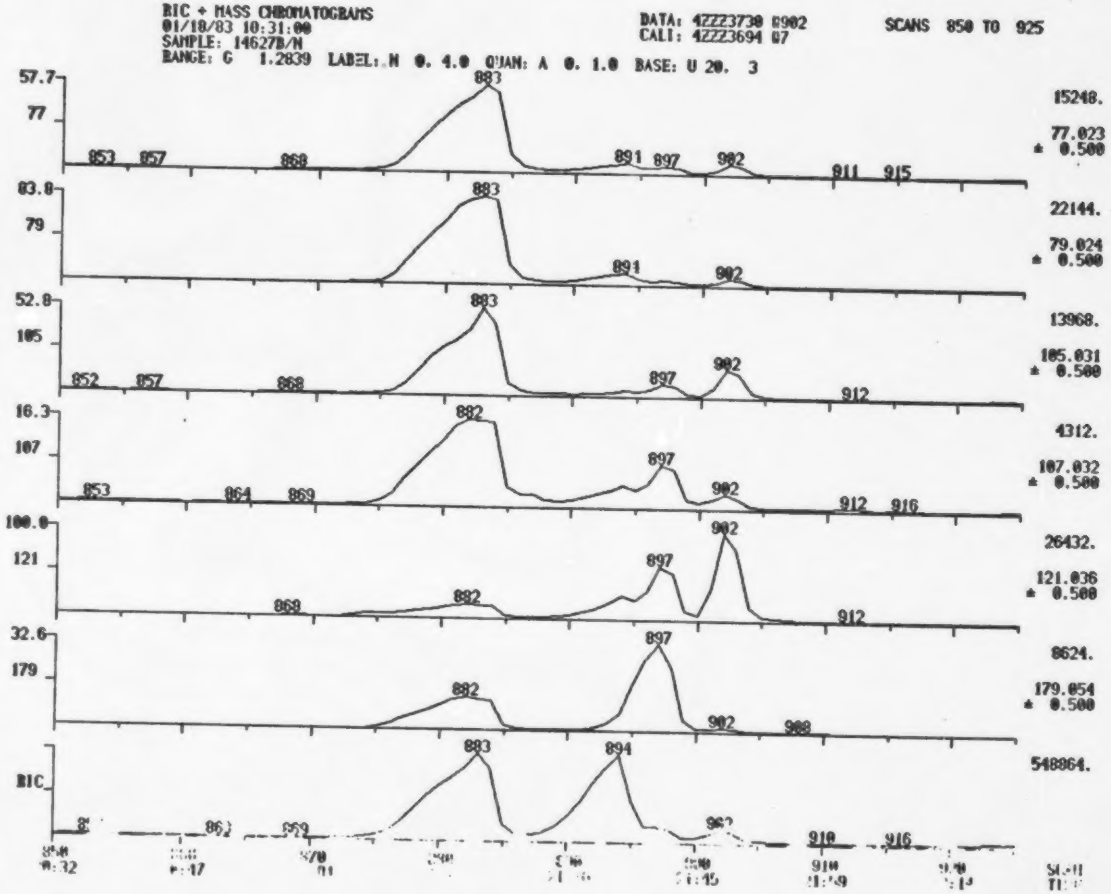


Figure 5.24. Extract 14627 (base/neutral), organic chemicals industry. Ion chromatogram of the major ions in the mass spectrum of the compound of interest: m/z 77, 79, 105, 107, 121, 179.

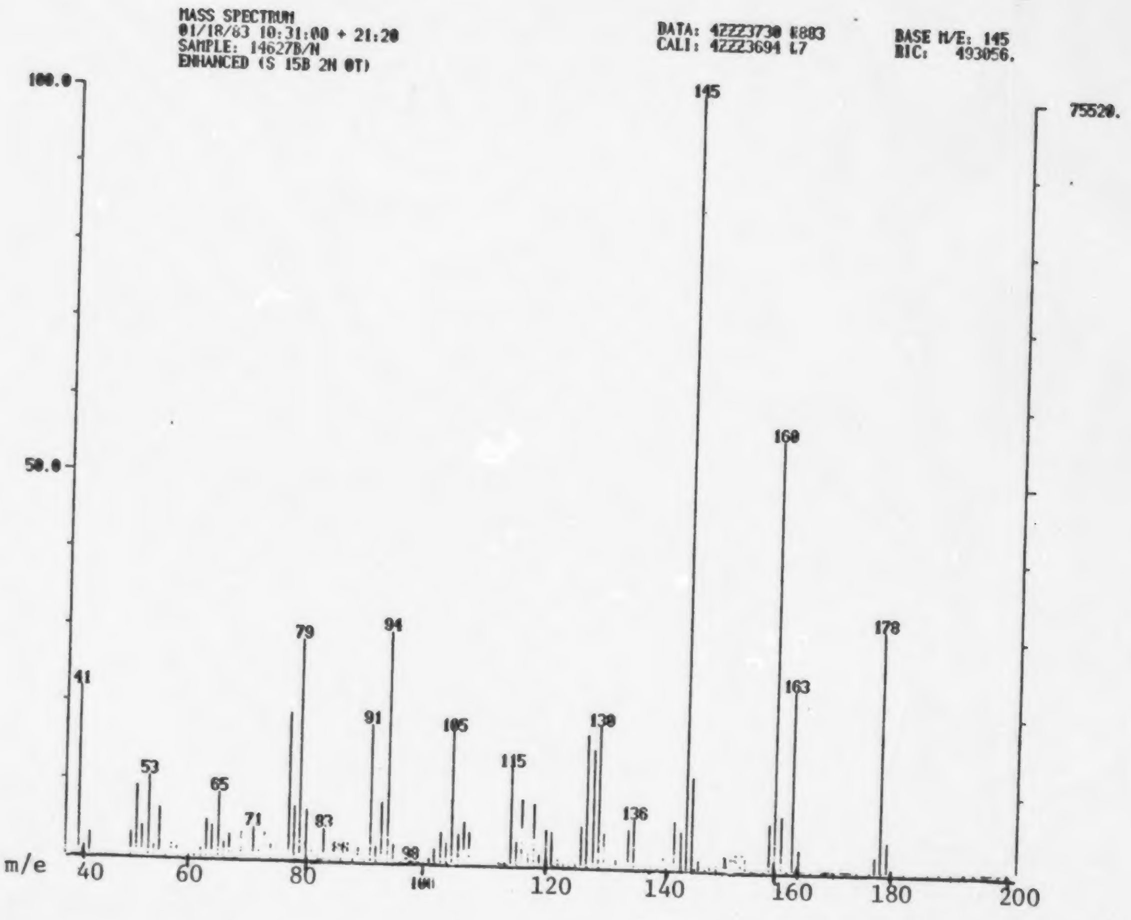


Figure 5.25. Mass spectrum similar to EPA compound of interest.

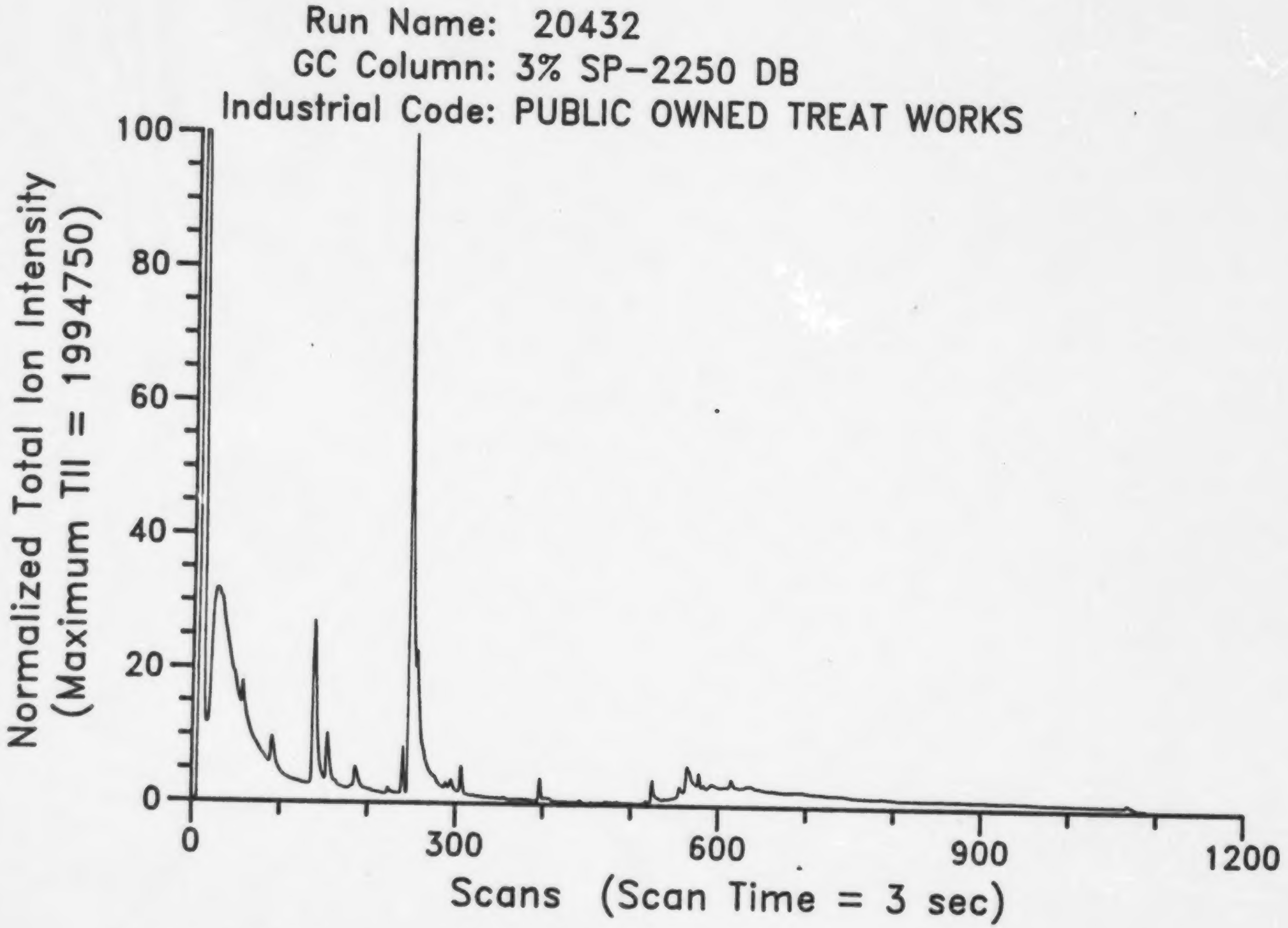


Figure 5.26. Packed column chromatogram of extract 20432 (base/neutral), publicly owned treatment works.

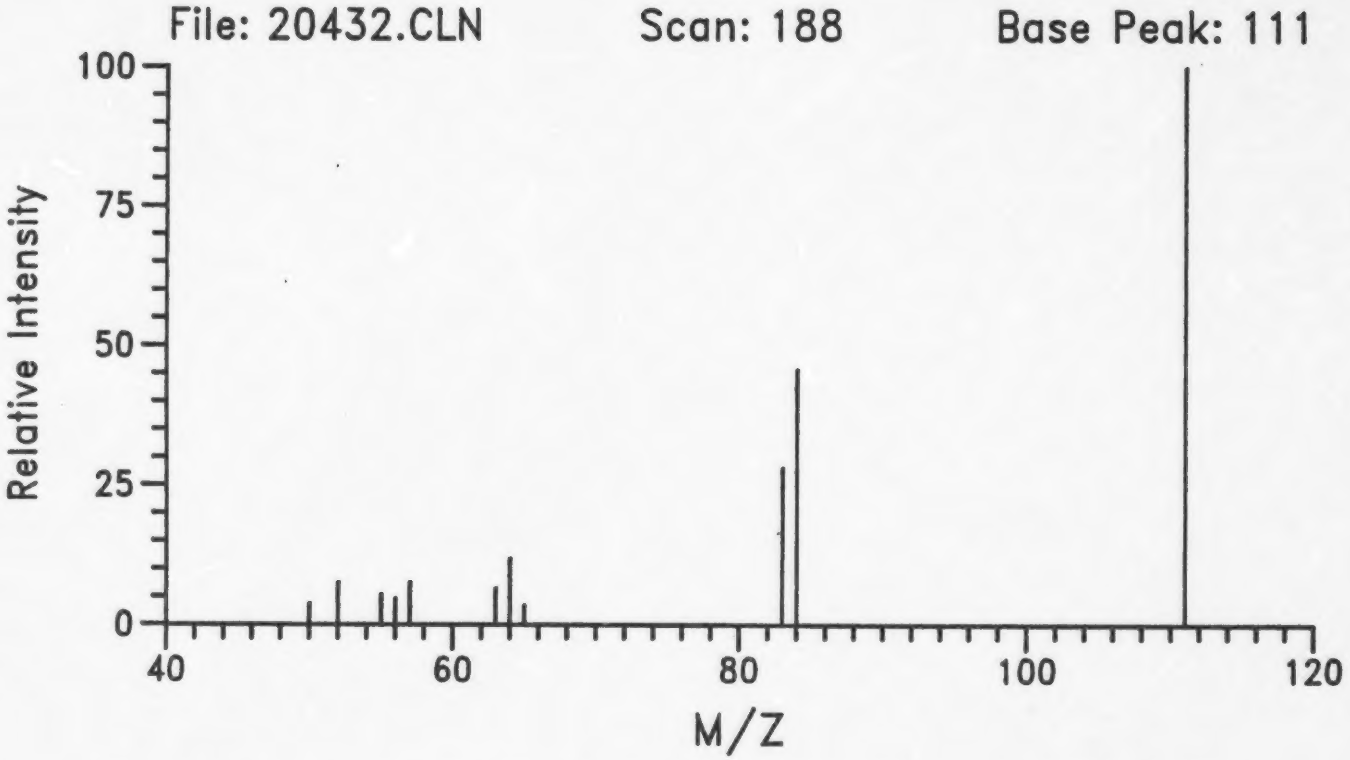


Figure 5.27. Extract 20432 (base/neutral), publicly owned treatment works. Frequency of occurrence: 19.

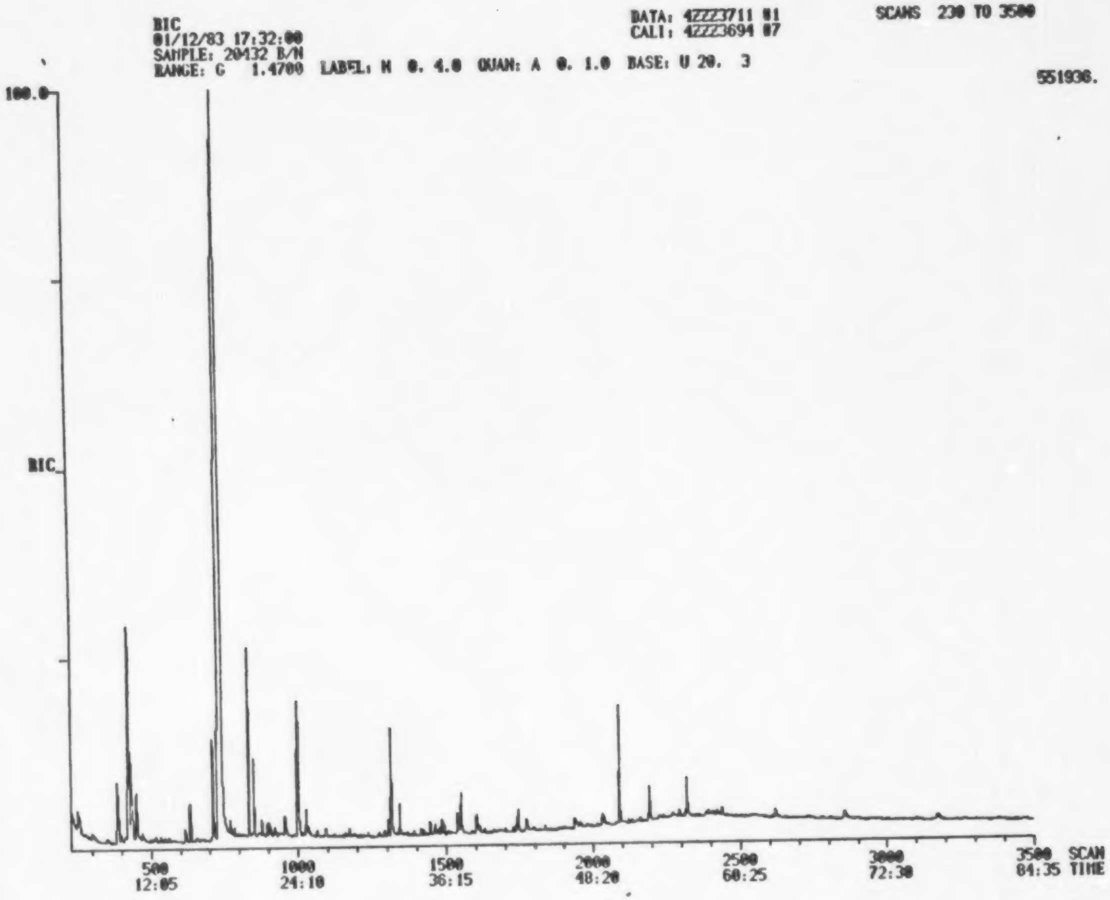


Figure 5.28. Capillary chromatogram of extract 20432 (base/neutral), publicly owned treatment works.

peaks of the spectrum provided by the Environmental Protection Agency is shown in Figure 5.29. The ion chromatogram suggests the possible occurrence of the compound of interest at three locations, spectrum number 474, 943, and 1002. Spectrum number 1002 corresponds to the mass spectrum of the standard, 2-fluorobiphenyl. The other two mass spectra are shown in Figures 5.30 and 5.31. The mass spectrum shown in Figure 5.30 can readily be seen to have only a superficial correspondence to the mass spectrum of the compound of interest; in fact, this spectrum appears to be the mass spectrum of a dichlorobenzene isomer. The mass spectrum shown in Figure 5.31 has a closer similarity to the mass spectrum of the compound of interest but is obviously not identical since the most intense peak of the mass spectrum in this Figure is $\underline{m}/\underline{z}$ 139. No further analytical efforts were made on this extract.

TABULATED INFORMATION FOR EXTRACTS

In 40-50 cases, work on extracts was abandoned at early stages. In several instances, a single capillary gas chromatographic analysis with low resolution mass spectrometry was sufficient to disclose that the compound of interest could not be found. In a few of the cases, analysis was pursued further but then abandoned for other reasons. In still other cases, a mass spectrum similar to, but not exactly like, the compound of interest was observed. In cases of fairly close but not identical correspondence, there is always the strong possibility that the enhanced chromatographic resolution has deconvoluted co-eluting components and that now a mass spectrum corresponding exactly to the one originally obtained can no longer be observed. The extracts are described in Table 5.1; mass spectra of components of interest are presented in Appendix A. The disposition of the extracts is described in Table 5.1. There are a few possible outcomes, as presented in Table 5.1:

1) spectrum only similar. No exact match to the mass spectrum supplied by the Environmental Protection Agency was observed. Either key peaks were missing or ratios between peaks were not correct.
2) no similar spectrum found. In all of the chromatogram, no spectrum corresponding to any degree to the spectrum of interest could be observed.

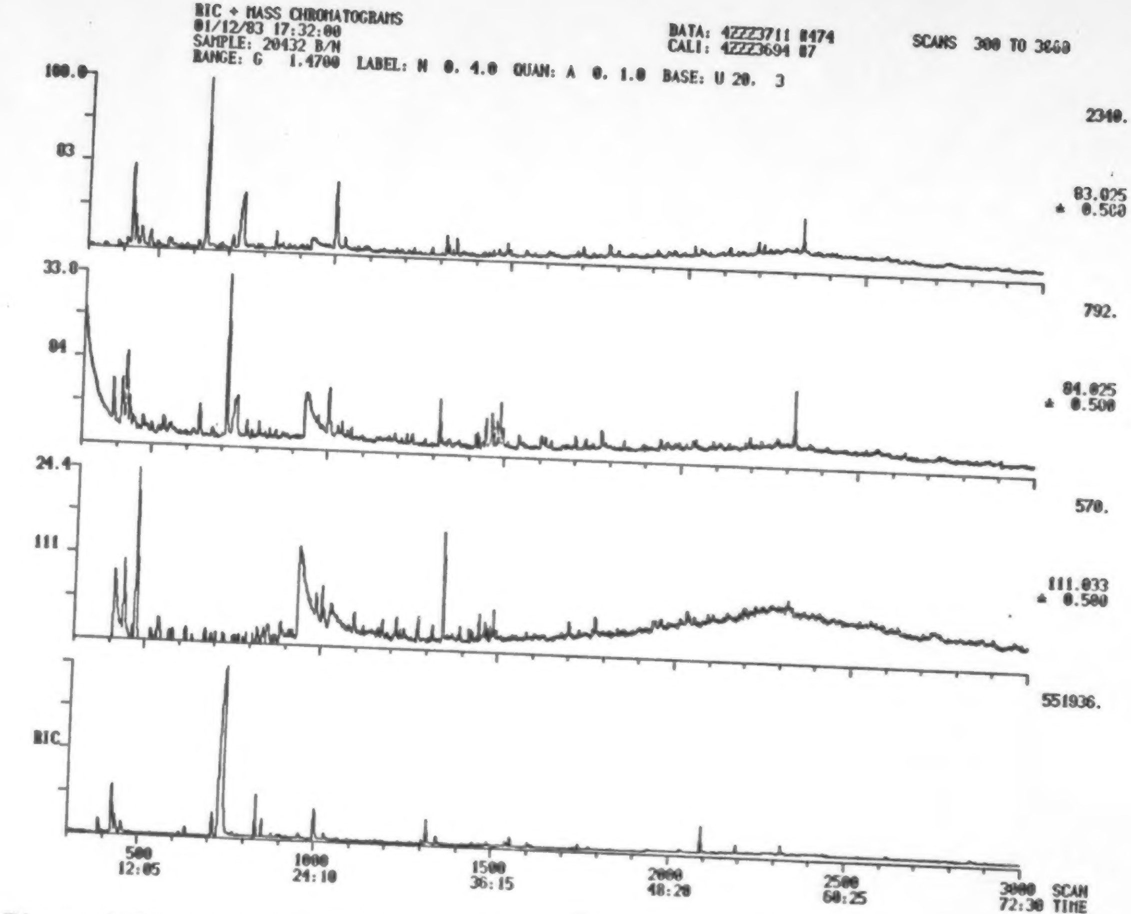


Figure 5.29. Extract 20432 (base/neutral), publicly owned treatment works. Ion chromatogram of m/z 83, 84 and 111.

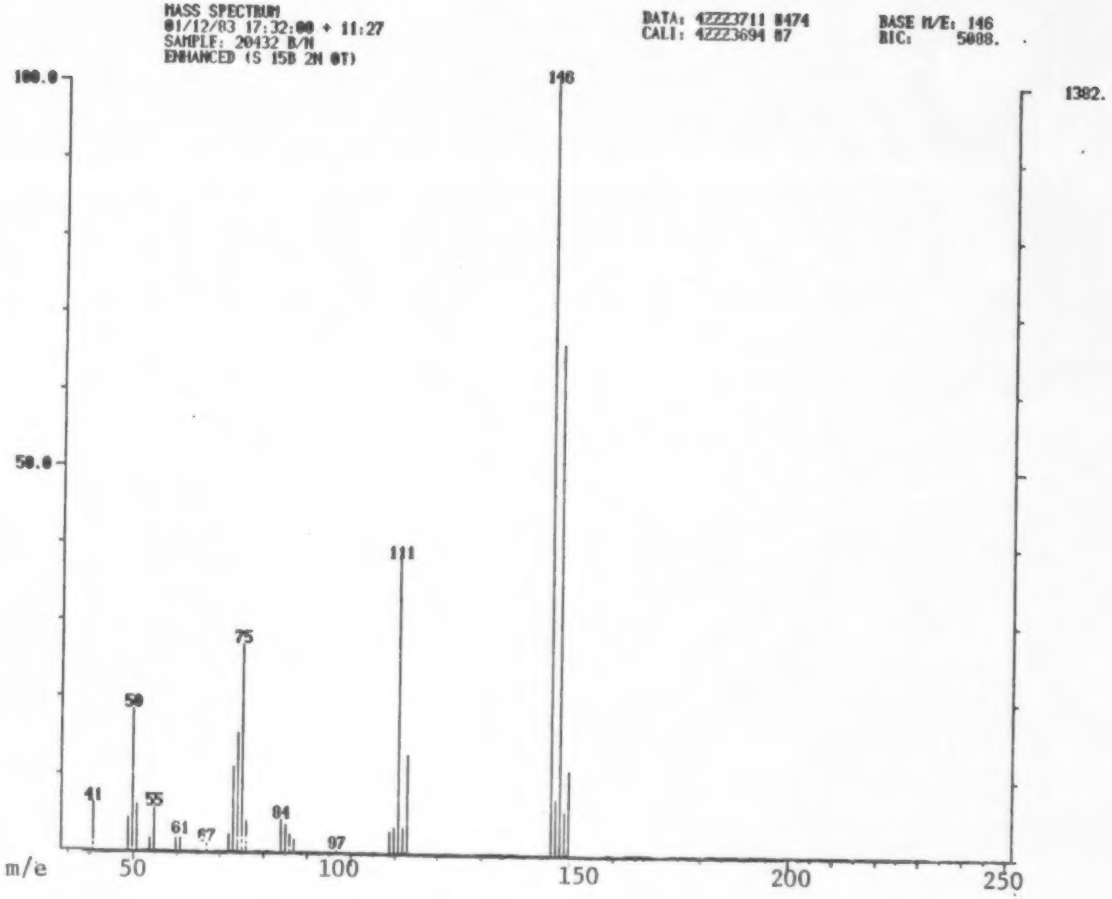


Figure 5.30. Mass spectrum similar to EPA compound of interest.

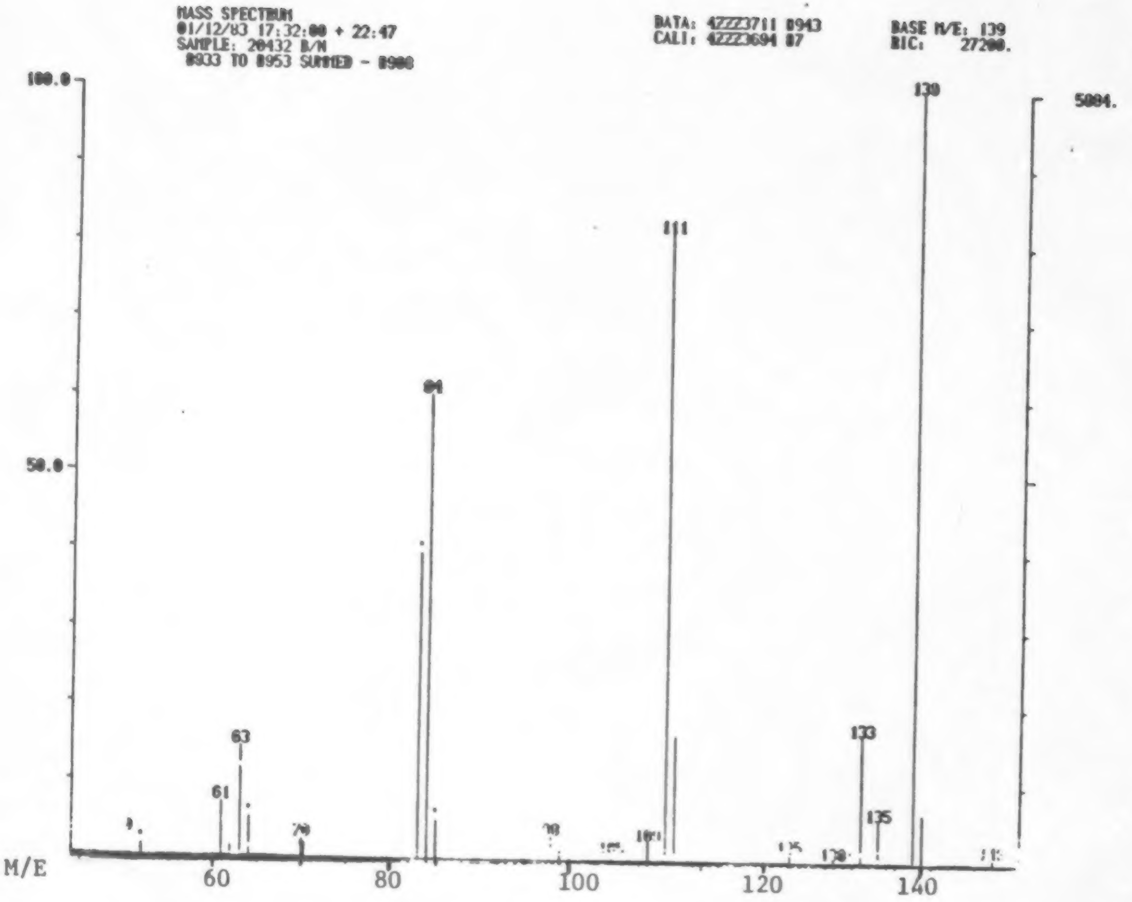


Figure 5.31. Mass spectrum similar to EPA compound of interest.

3) relatively detailed discussion of special circumstances. There were times, for instance, when a tentative identification of the compound of interest could be made by inspection of the mass spectrum supplied. The question in this case becomes why the computer could not make an identification in the original analysis. At other times, an apparently successful computerized library identification could be made from the spectrum obtained from the capillary analysis.

EXTRACTS SUBJECTED TO THE LABORATORY CLEANUP PROCESS

After an initial capillary chromatogram had been obtained, the compound of interest was observed, and accurate mass measurements had been made, ten of the industrial effluent extracts were subjected to a laboratory cleanup process as described in the experimental section. The extracts were selected for this process because the compound of interest seemed to be polar (as evidenced from the presence of heteroatoms such as nitrogen and oxygen) observed over an extensive background of hydrocarbons. The compound of interest could usually be separated from this hydrocarbon background and could then be observed in a more polar fraction with a far lower background level. In order to evaluate the cleanup process, several of the major peaks observed in each fraction were characterized by computerized library search. Frequently, the presence of several polar compounds was not evident from the original chromatogram. Each of the extracts is discussed individually since each represents the combination of several levels of analytical effort; results are summarized in Table 5.2.

Extract 584 (Acid), Pulp and Paper Industry, Caustic Extract Stage

The packed column chromatogram of extract 584 (acid) is shown in Figure 5.32. The mass spectrum of the compound of interest is presented in Figure 5.33 The capillary chromatogram of extract 584 is shown in Figure 5.34. The mass spectrum of the compound of interest as obtained from the capillary chromatogram is shown in Figure 5.35. The quality of the computerized library search identification does not produce a confident identification, as shown in Figure 5.36. The computerized library search does not even provide clear guidance as to the type of compound which might be present since the choices range from a hydrocarbon to

Table 5.2. Analysis of Industrial Effluent Extracts

Sample	Industry	Analytical Efforts	Conclusion
584 (Acid)	Pulp and Paper	Capillary analysis	Compound of interest found
		Accurate mass measurement	Possibilities narrowed to two
		Laboratory cleanup	Compound of interest lost
7367 (Base/ Neutral)	Amusements and Athletic Goods	Capillary analysis	Compound of interest found
		Accurate mass measurement	One possibility
		Laboratory cleanup	Compound of interest lost
8212 (Base/ Neutral)	Timber Products	Capillary analysis	Several spectra of compounds of interest
		Accurate mass measurement	Several possibilities
		Laboratory cleanup	Compounds of interest distributed among fractions; clean spectra obtained
11533 (Base/ Neutral)	Organics and Plastics	Capillary analysis	Compound of interest found
		Accurate mass measurement	Many possibilities; could not select one
		Laboratory cleanup	Compound of interest lost
12245 (Base/ Neutral)	Timber Products	Capillary analysis	Compound of interest found
		Accurate mass measurement	Four possibilities
		Laboratory cleanup	Compound found in fraction 2 as a minor constituent
12316 (Base/ Neutral)	Timber Products	Capillary analysis	Compounds of interest found
		Accurate mass measurement	Two possibilities
		Laboratory cleanup	One spectrum deconvoluted, other constituent lost
13230 (Acid)	Mechanical Products	Capillary analysis	Compound of interest found
		Accurate mass measurement	Multiple possibilities
		Laboratory cleanup	Two related compounds in fraction 2

Table 5.2 (continued)

Sample	Industry	Analytical Efforts	Conclusion
		Chemical ionization mass spectrometry (methane)	Either $(M+H)^+$ or $(M-H)^+$ observed at m/z 291 Probable composition; no tentative structure
13240 (Base/ Neutral)	Mechanical Products	Capillary analysis Accurate mass measurement Laboratory cleanup Chemical ionization mass spectrometry (methane)	Compound of interest found Multiple possibilities Two related compounds in fraction 2 Either $(M+H)^+$ or $(M-H)^+$ observed at m/z 291 Probable composition; no tentative structure
13248 (Base/ Neutral)	Mechanical Products	Capillary analysis Accurate mass measurement Laboratory cleanup	Compound of interest found Multiple possibilities Several related compounds in fraction 2
		Chemical ionization mass spectrometry (PPINICI), methane	$(M\pm H)^{+\text{ or }-}$ at 291, 305, 347
19436 (Acid)	Plastic and Synthetics	Capillary analysis Accurate mass measurement Laboratory cleanup	Compound of interest found $C_9H_{20}O_3$ only possibility Compound of interest lost
21258 (Base/ Neutral)	Aluminum	Capillary analysis Accurate mass measurement Laboratory cleanup	Compound of interest found Three possibilities Compound of interest in second and third fractions; minor constituent

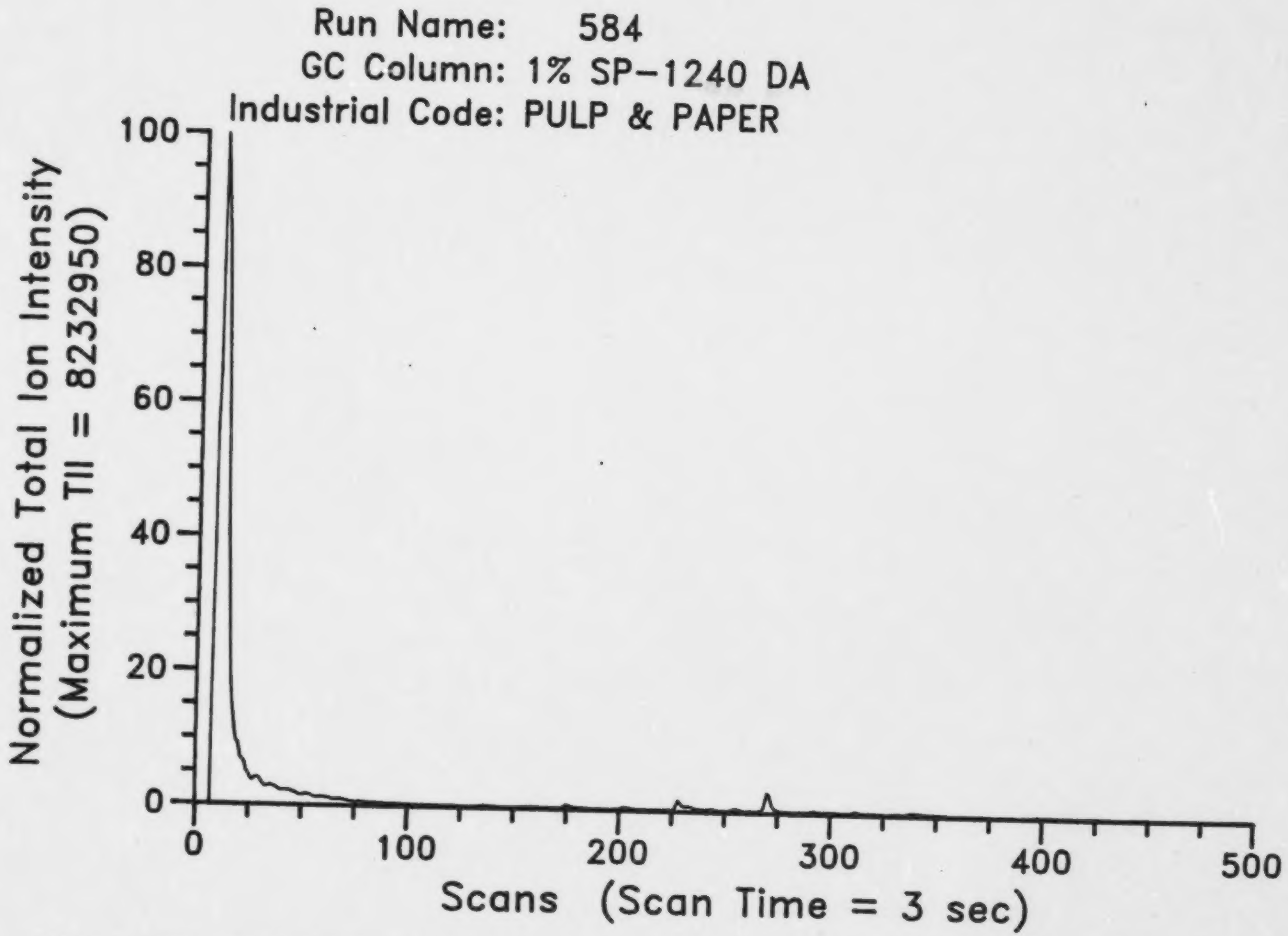


Figure 5.32. Packed column chromatogram, extract 584 (acid), pulp and paper industry.

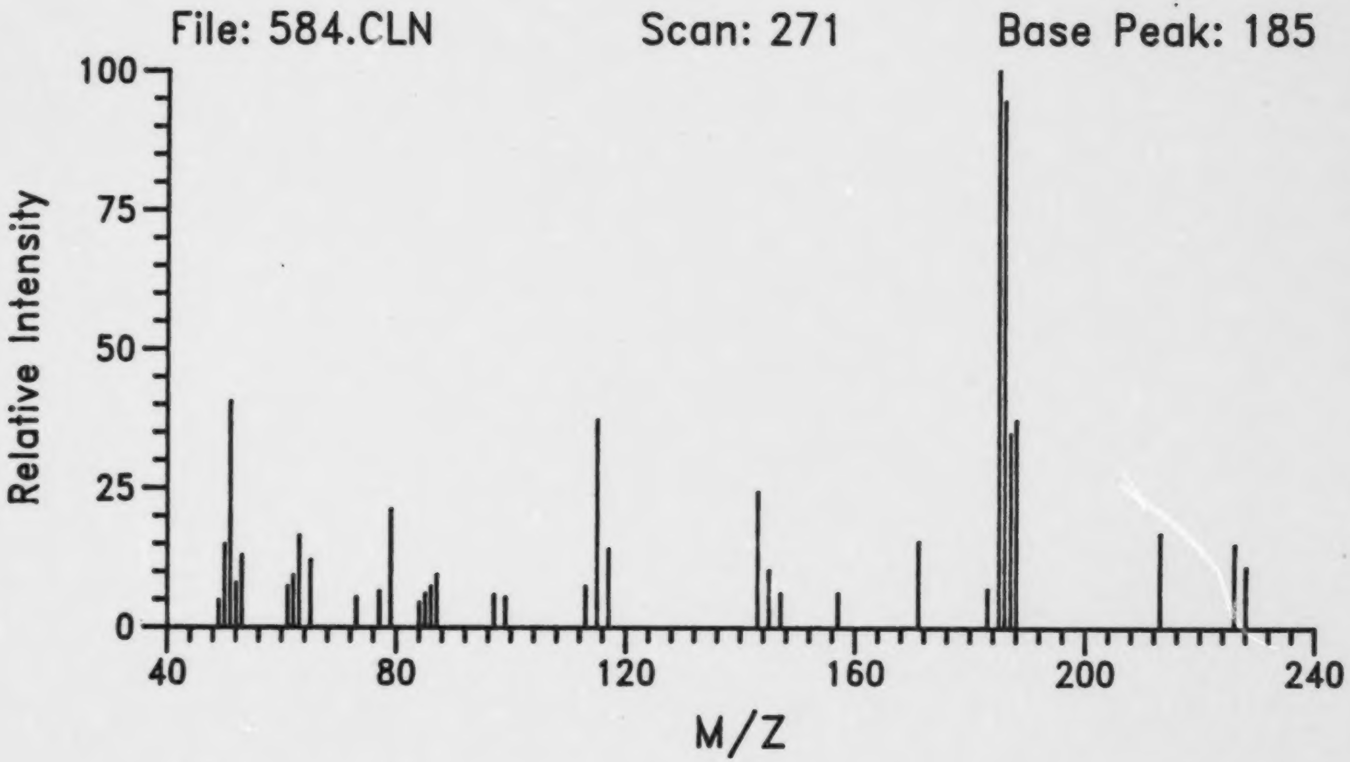


Figure 5.33. Extract 584 (acid), pulp and paper industry. Frequency of occurrence: 9.

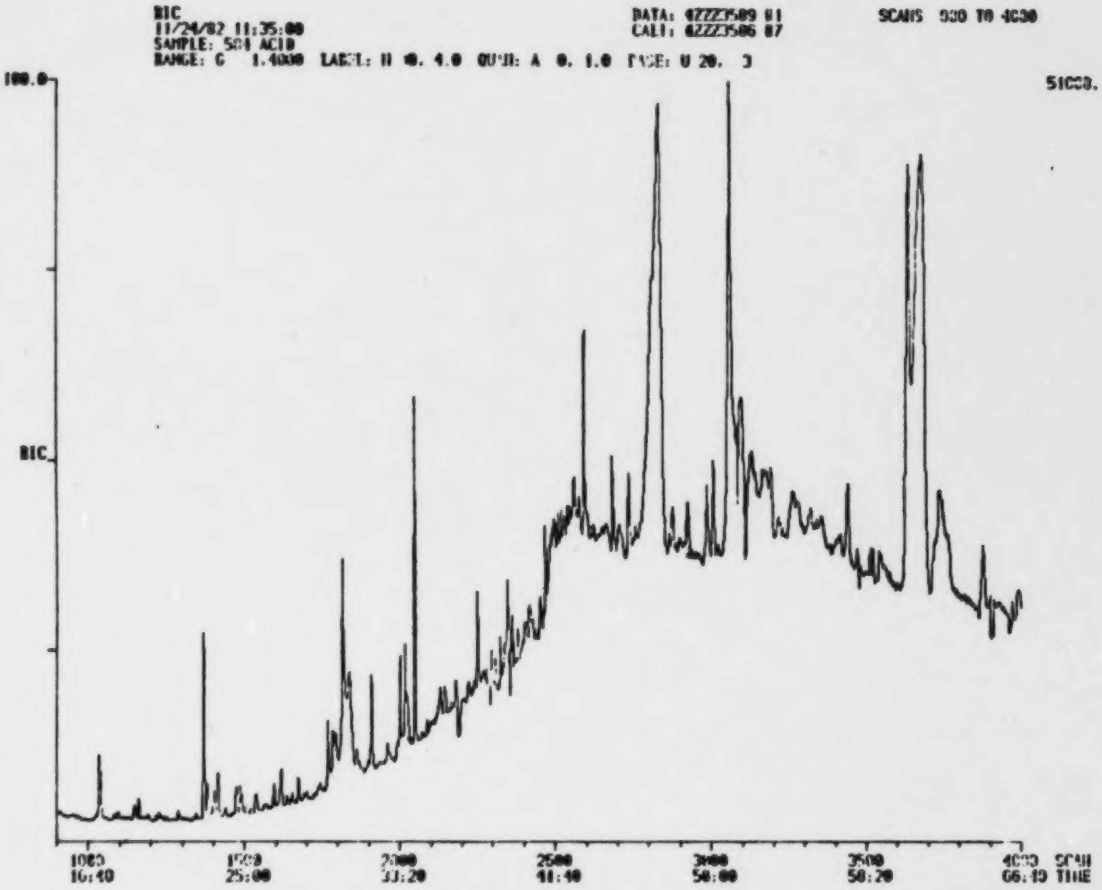


Figure 5.34. Capillary chromatogram of extract 584 (acid), pulp and paper industry.

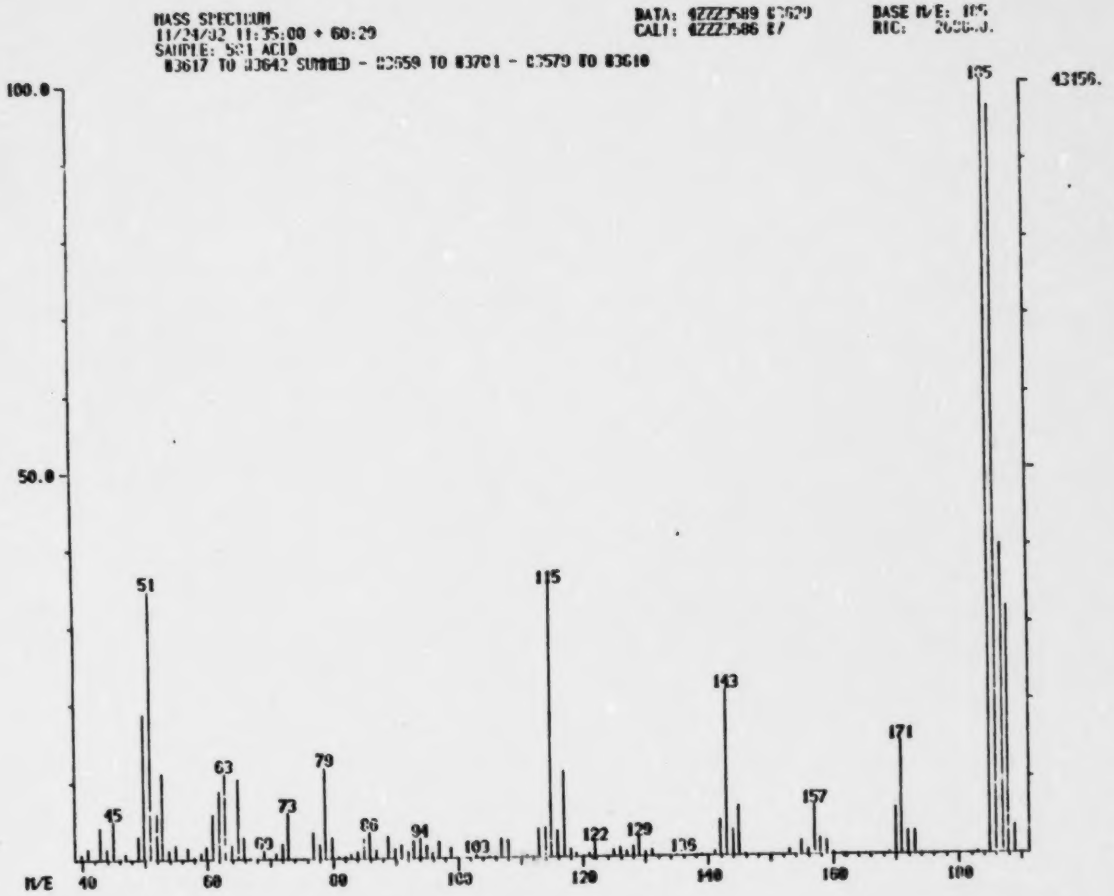


Figure 5.35. Mass spectrum of EPA compound of interest, extract 584 (acid), pulp and paper industry

Figure 5.36. Computerized library search, scan #3629, extract 584 (acid).

```
LIBRARY SEARCH                DATA: 42ZZ3589 #3629      BASE M/E:  186
11/24/82 11:35:08 + 60:29     CALI: 42ZZ3586 #   7      RIC:    254207.
SAMPLE: 584 ACID
 #3617 TO #3642 SUMMED - #3659 TO #3704 - #3579 TO #3610

25419 SPECTRA IN LIBRARYNB SEARCHED FOR MAXIMUM PURITY
  157 MATCHED AT LEAST 4 OF THE 16 LARGEST PEAKS IN THE UNKNOWN

RANK IN NAME
1  8629 CYCLOHEXANONE,2-(PHENYLMETHYLENE)-
2 22736 SULFONIUM,(CYANOAMINO)DIPHENYL-,HYDROXIDE,INNERSALT
3  1695 BENZENE,1,1'-THIOBIS-
4  9401 CYCLOHEPT\F\INDENE,1,2.3,5.6,7,8,9-OCTAHYDRO-
5 17317 1-NAPHTHOL,2,5,8-TRIMETHYL-

RANK  FORMULA                              M.WT B.PK   PURITY    FIT   RFIT
1 C13.H14.O                                 186  186      598    857    634
2 C13.H10.N2.S                              226  186      558    739    640
3 C12.H10.S                                 186  186      543    739    656
4 C14.H18                                   186  186      521    675    573
5 C13.H14.O                                 186  186      503    697    502
```

oxygen-, sulfur-, or nitrogen- and sulfur-containing. Accurate mass measurement was performed for three ions of the mass spectrum, and several viable possibilities were found after chemical impossibilities and compositions for which there was no logical transition were eliminated. Table 5.3 lists the possible compositions with the error in millimass units. Many possibilities have already been eliminated as chemically or mass spectrometrically impossible. If the permissible error is restricted to 5 millimass units, only three possibilities remain viable. The mass spectrum appears to show the presence of chlorine, so the possibilities are further limited to two, $C_8H_7O_3Cl$ or $C_5H_{11}SO_3Cl$. The mass spectrum certainly suggests that a methyl group and an ethyl group are present in the molecule. The loss of 43 mass units as C_2H_3O argues for the presence of an acetyl group. A laboratory cleanup was attempted (see Figures 5.37 and 5.38), but when the fractions were reexamined, the compound of interest could no longer be found. The original chromatogram was reexamined to assess the extent of the hydrocarbon background (see Figure 5.39), and the amount of hydrocarbon contribution to the total complex background appears to be small. The peaks shown in the chromatograms of the fractions are siloxanes of various sorts (see Figures 5.40 and 5.41). Without more definitive information about the nature of the oxygen-containing functional groups (only one of three possible oxygen atoms is accounted for by the presence of an acetyl group), assignment of a structure is not possible. Use of GC/FTIR over the extensive background observed in the original chromatogram would be unfruitful.

Extract 7367 (Base/Neutral), Amusements and Athletic Goods Industry, Barrel Finish

The packed column chromatogram of extract 7367 (base/neutral) is shown in Figure 5.42. The mass spectrum of the compound of interest is presented in Figure 5.43. The capillary chromatogram of extract 7367 is shown in Figure 5.44. The mass spectrum of the compound of interest as obtained from the capillary chromatogram is shown in Figure 5.45. The hydrocarbon background in the region of elution of the compound of interest is so prevalent that it is impossible, using background subtraction techniques, to obtain a clean mass spectrum. Even above the background,

Table 5.3. Accurate mass measurement, extract 584 (acid)

Observed mass: 186.0127

Possible Composition	Error (mmu)
$C_{11}H_6SO$	1.2
$C_8H_{10}S_2O$	4.6
$C_7H_6O_6$	3.7
$C_3H_{10}S_2O_3N_2$	0.6
$C_8H_7O_3Cl$	-4.3
$C_5H_{11}SO_3Cl$	-1.0

Observed mass: 185.0049

Possible Composition	Error (mmu)
$C_{11}H_5SO$	1.2
$C_8H_9S_2O$	4.6
$C_7H_5O_6$	3.7
$C_3H_9S_2O_3N_2$	0.5
$C_8H_6O_3Cl$	-4.4
$C_5H_{10}SO_3Cl$	-1.0

Observed mass: 142.9903

Possible Composition	Error (mmu)
C_9H_3S	5.2
$C_6H_7S_2$	8.6
$C_5H_3O_5$	7.7
$CH_7S_2O_2N_2$	4.6
$C_6H_4O_2Cl$	-0.3
$C_3H_8SO_2Cl$	3.0

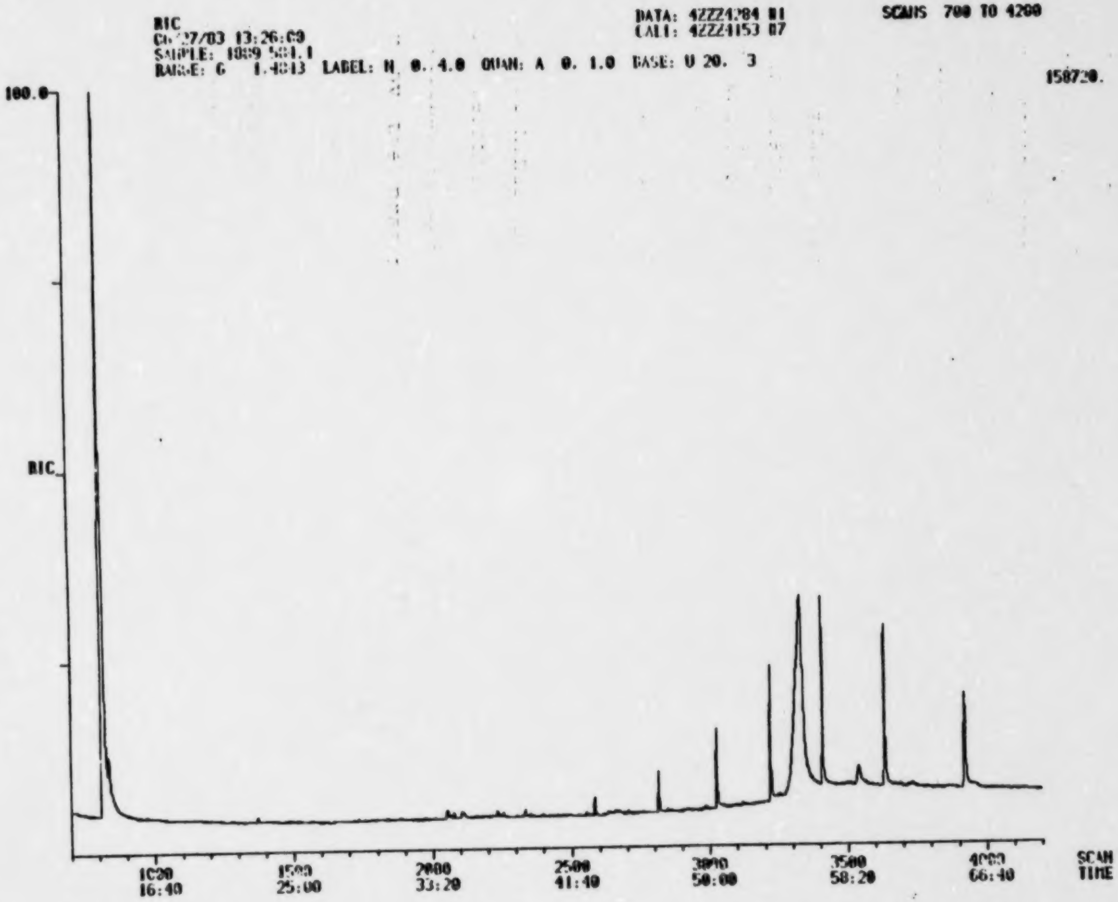


Figure 5.37. Capillary chromatogram of extract 584 (acid), fraction 1.

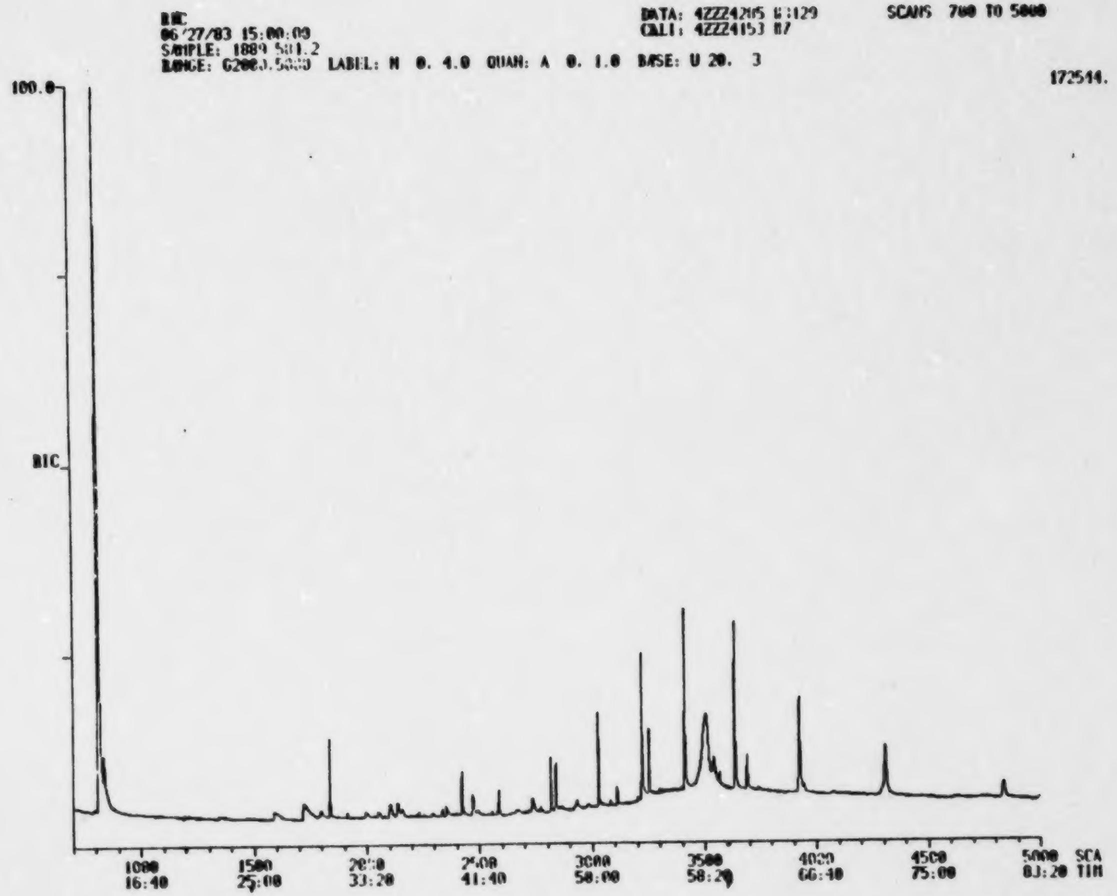


Figure 5.38. Capillary chromatogram of extract 584 (acid), fraction 2.

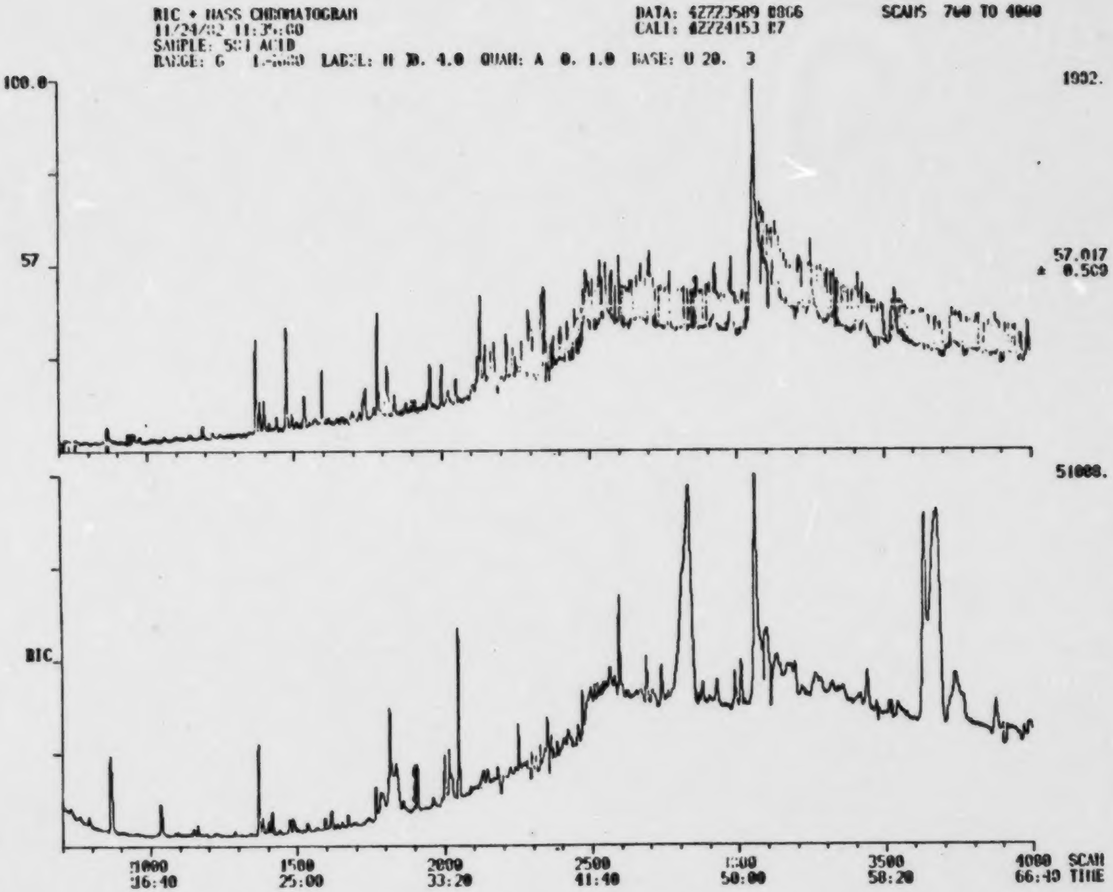


Figure 5.39. Extracted ion current profile of m/z 57 for extract 584 (acid), showing a minimal contribution of hydrocarbons to the background.

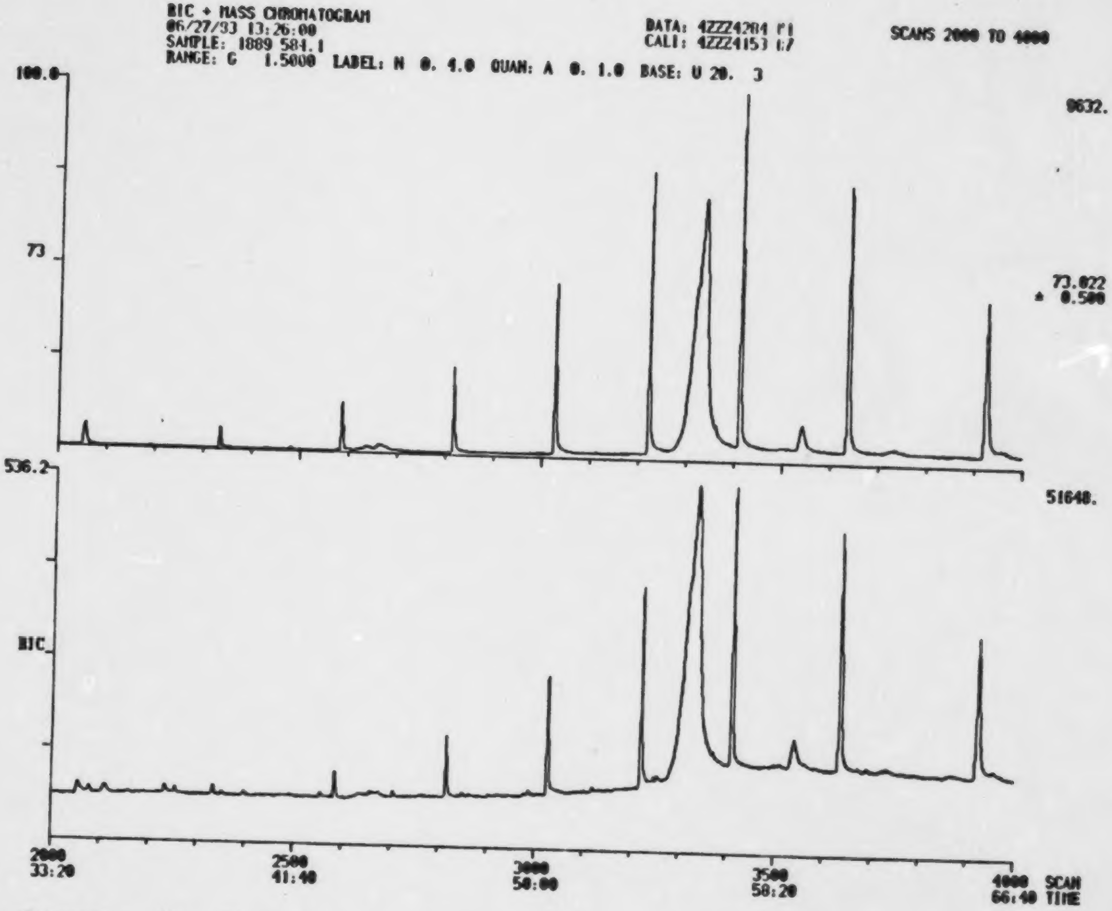


Figure 5. 40. Extracted ion current profile of m/z 73 (characteristic of siloxanes) for extract 584 (acid), fraction 1.

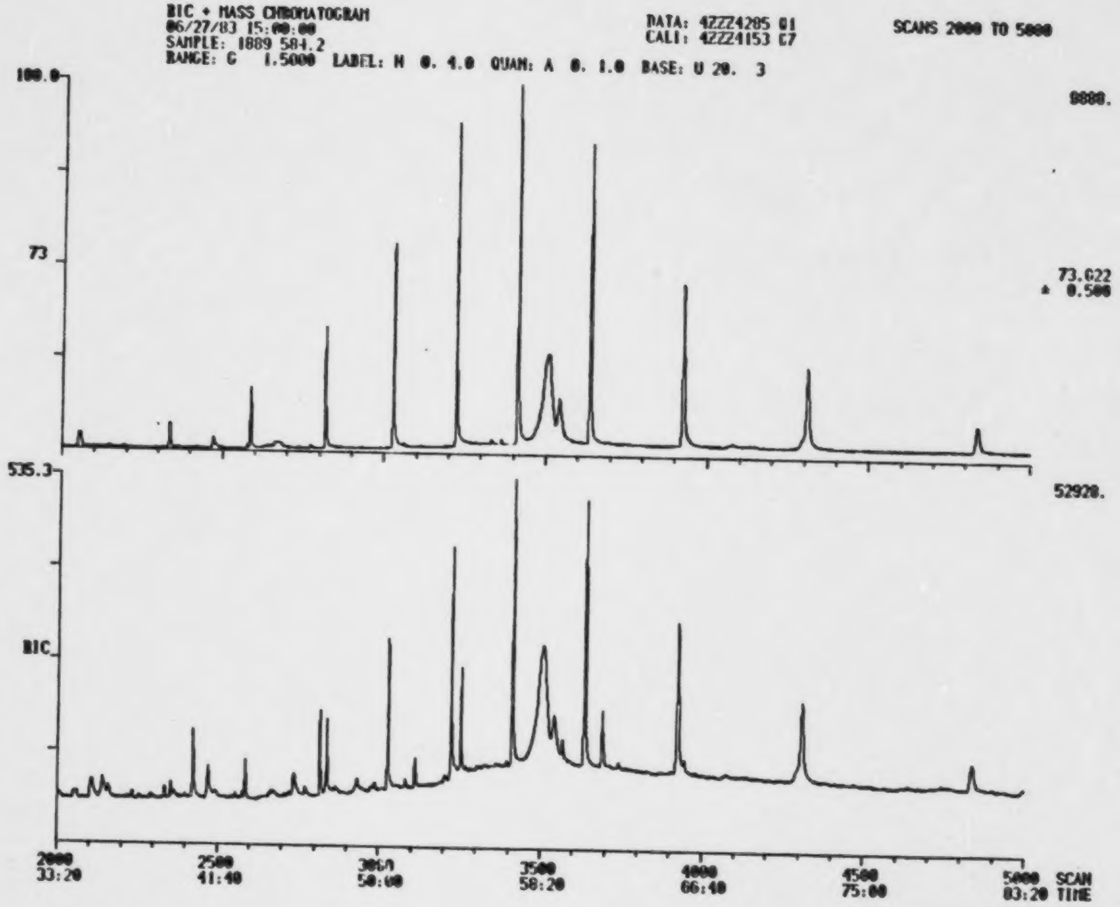


Figure 5.41. Extracted ion current profile of m/z 73 (characteristic of siloxanes) for extract 584 (acid), fraction 2.

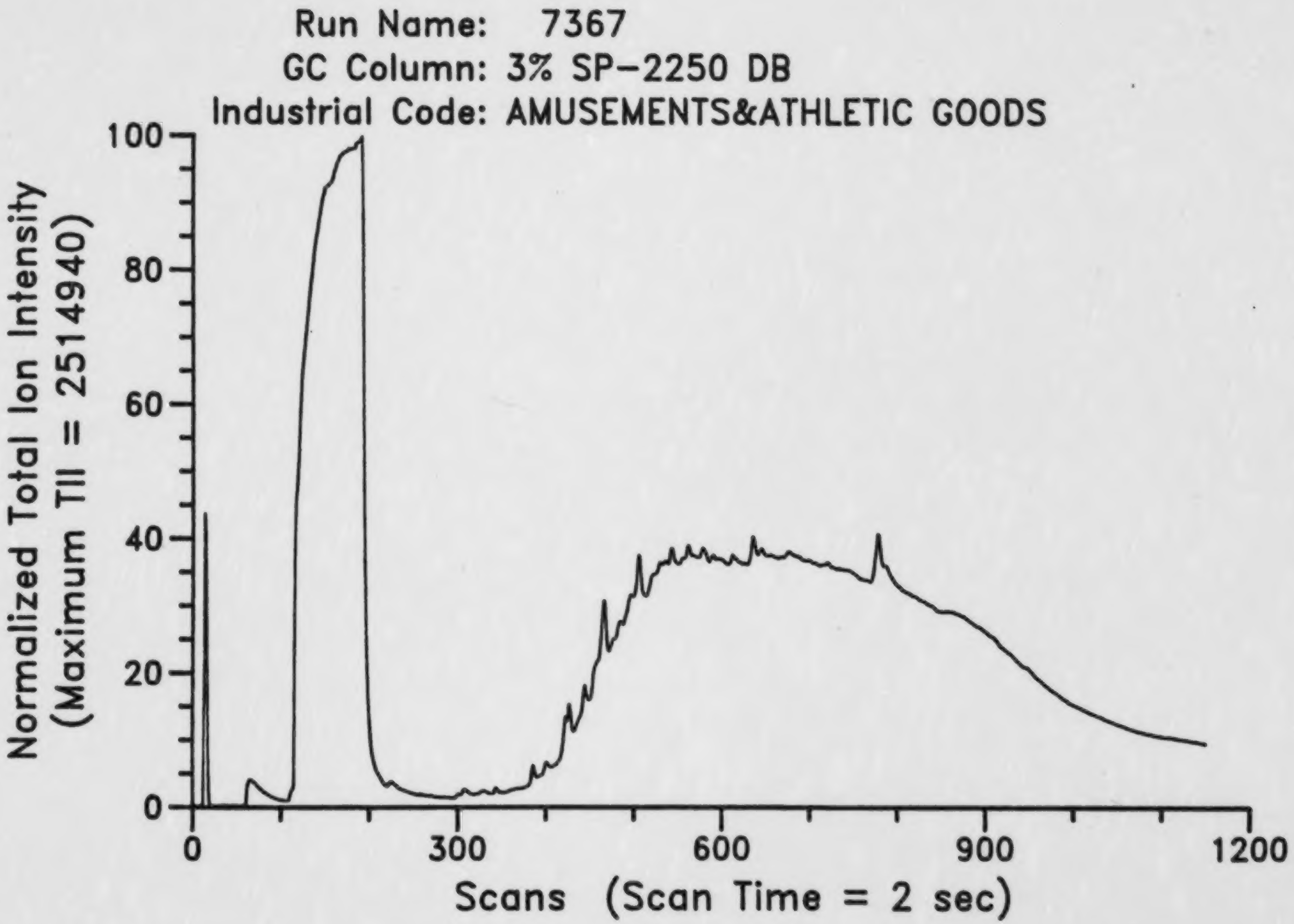


Figure 5.42. Packed column chromatogram, extract 7367 (base/neutral), amusements and athletic goods industry.

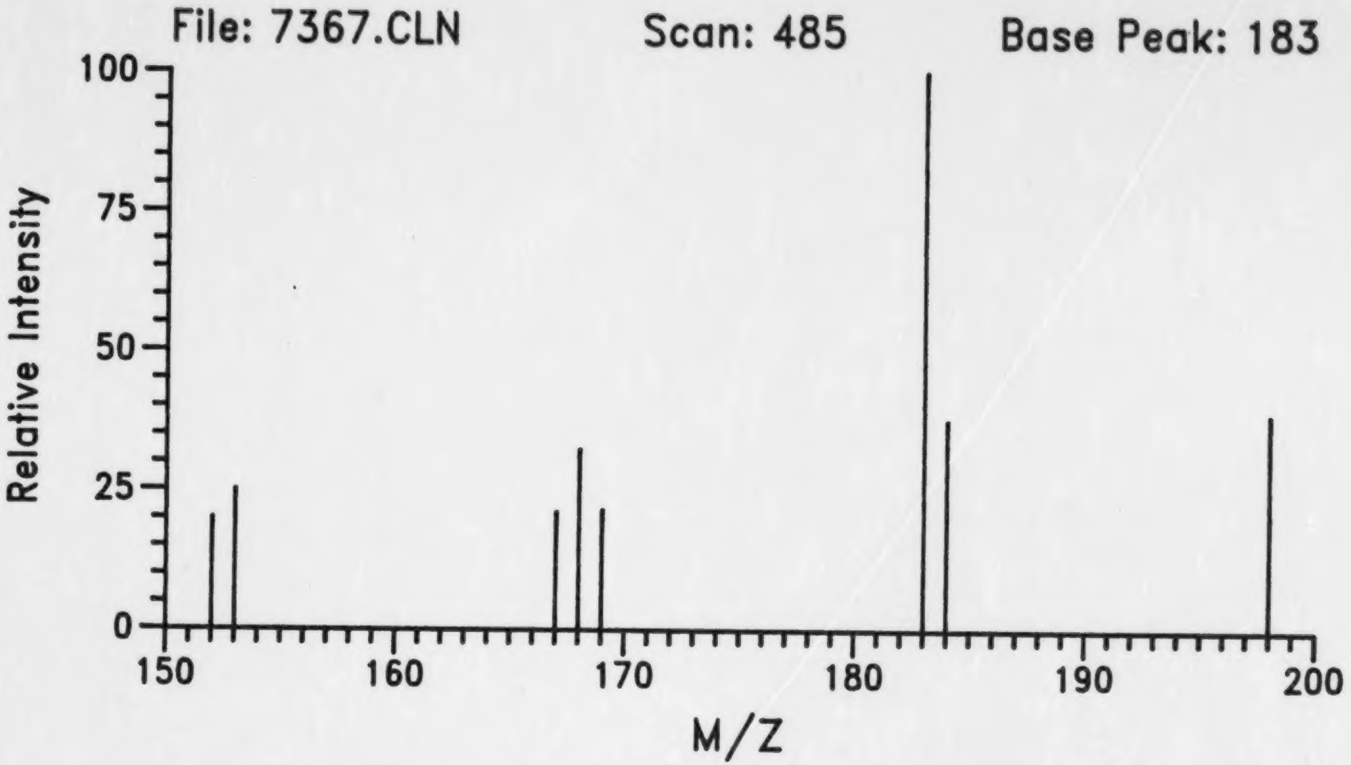


Figure 5.43. Extract 7367 (base/neutral), amusements and athletic goods industry. Frequency of occurrence: 10.

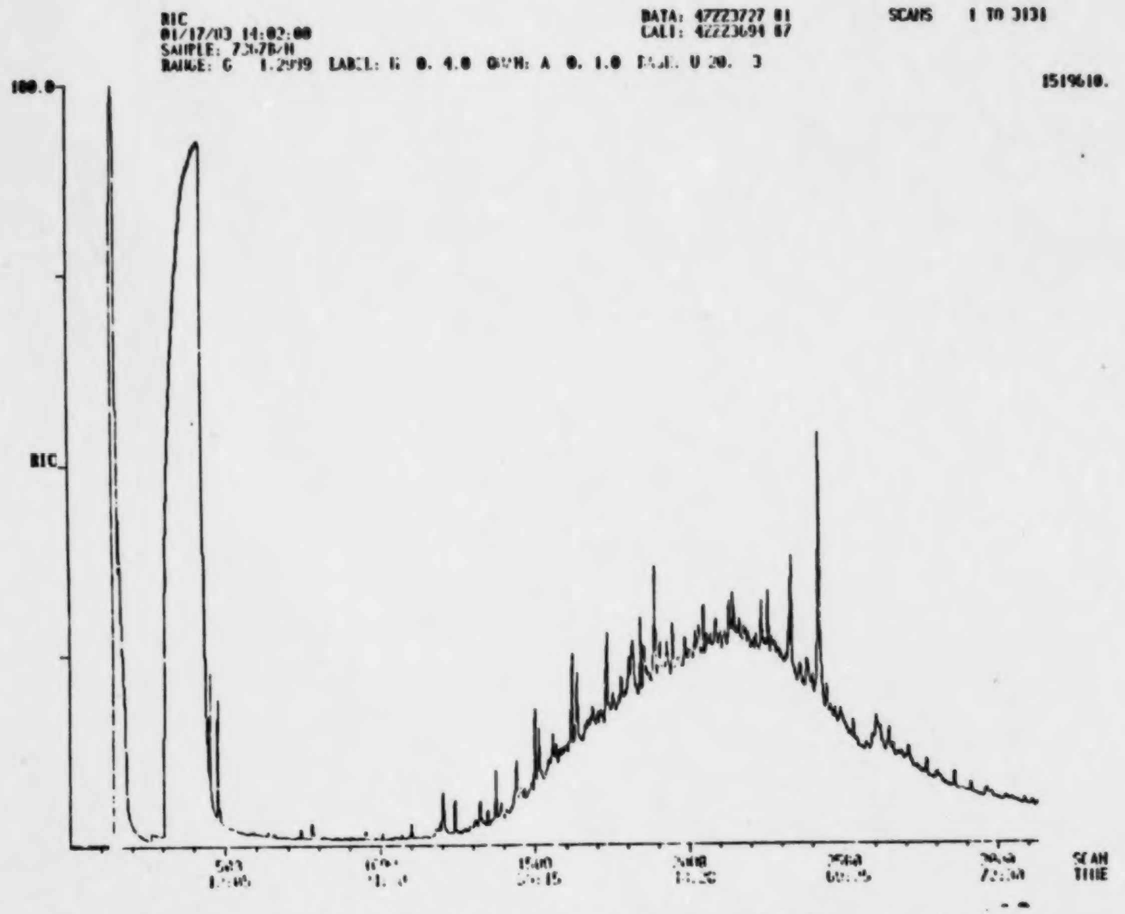


Figure 5.44. Capillary chromatogram of extract 7367 (base/neutral), amusements and athletic goods industry.

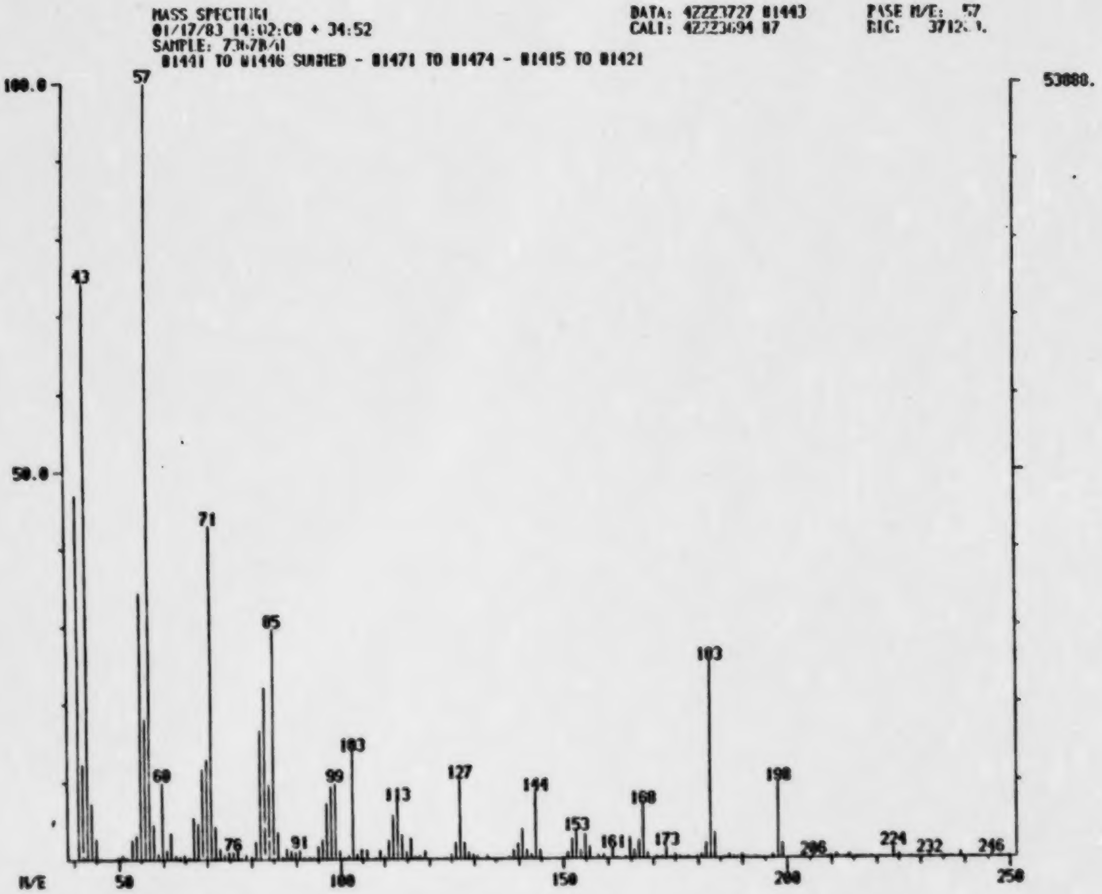


Figure 5.45. Mass spectrum of EPA compound of interest, extract 7367 (base/neutral), amusements and athletic goods industry, scan #1443.

it was possible to perform an accurate mass measurement, and the possibilities could be narrowed to one, $C_9H_{18}N_4O$ (observed mass, 198.1517; error, -3.7 mmu; observed mass 183.1252; error -0.6 mmu). However, in the presence of so much background, it was impossible to discern structural features, so a laboratory cleanup was attempted. The capillary chromatograms of the three resulting fractions are presented in Figures 5.46-5.48. The mass spectrum of the compound of interest could no longer be found after the cleanup. However, a representative group of the major peaks in the chromatograms were characterized by computerized library search to indicate the types of compounds observed in each of the fractions (see Table 5.4). Fraction 1 obviously retains the major portion of the hydrocarbon background. There is still substantial spillover of hydrocarbons into fraction 2. Fraction 3 presents a vastly simplified chromatogram of several polar compounds which could not be discerned at all beneath the extensive hydrocarbon background. (Note: there was no extensive effort made to characterize the extracts or the resulting fractions completely. A few of the major peaks in each of the fractions were examined to provide an indication of the types of compounds to be expected. No critical assessment of computerized identifications has been made.)

Extract 8212 (Base/Neutral), Timber Products Industry, Kerr McGee Proc. Pond Inf.

The packed column chromatogram of extract 8212 (base/neutral) is shown in Figure 5.49. Mass spectra of several compounds of interest were supplied and are presented in Figures 5.50-5.54. In the capillary analysis, a mass spectrum corresponding to EPA spectrum #56 was not found. EPA spectrum #312 also represents a compound not found as such, but the spectrum appears to be a composite: the component of mass 168 could not be found, the component at 170 could correspond to a member of the trialkylnaphthalene series, and the trialkylnaphthalenes are extensively present. Scan #427 also represents a composite spectrum which can be deconvoluted (see Figures 5.55 and 5.56). Accurate mass measurement data for these compounds are consistent with an identification as methyldibenzothiophene ($\underline{m}/\underline{z}$ 198) and dibenzoheptafulvene ($\underline{m}/\underline{z}$ 204), but there

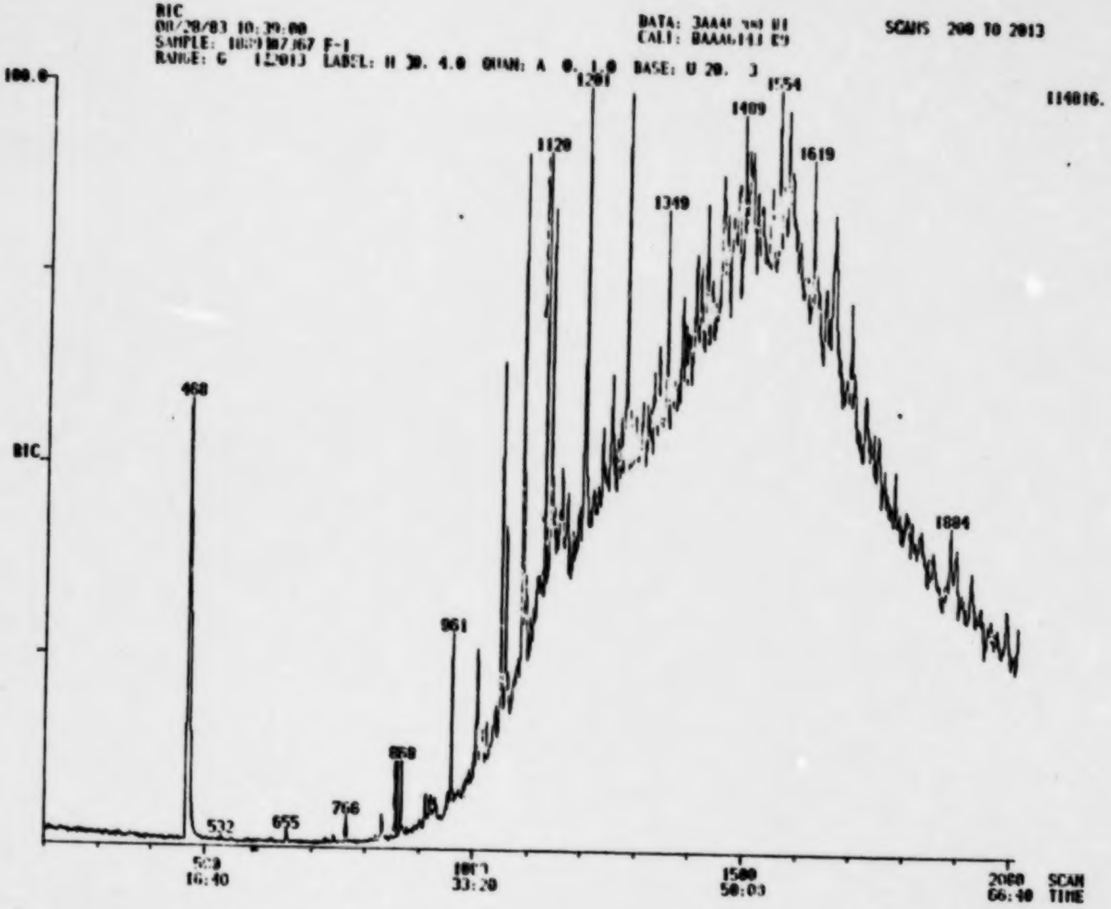


Figure 5.46. Capillary chromatogram of extract 7376 (base/neutral), fraction 2.

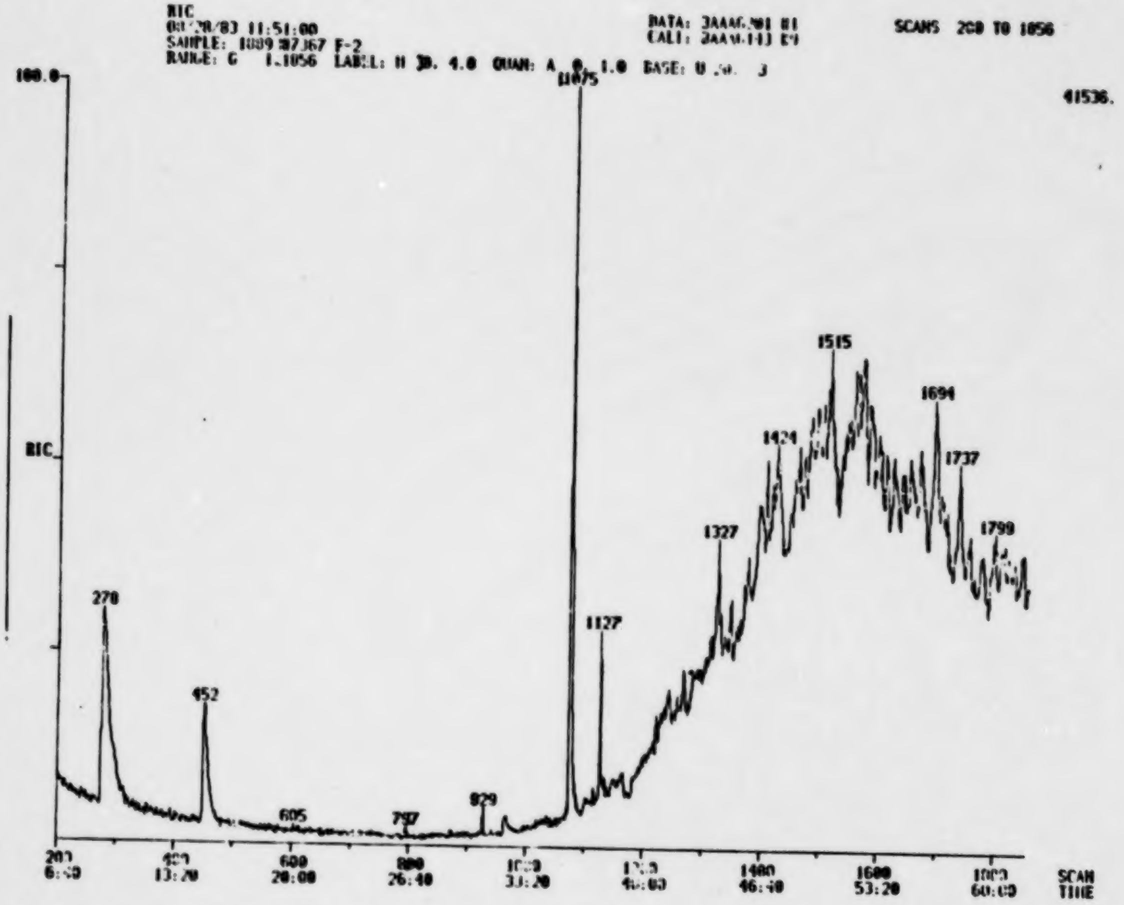


Figure 5.47. Capillary chromatogram of extract 7367 (base/neutral), fraction 2.

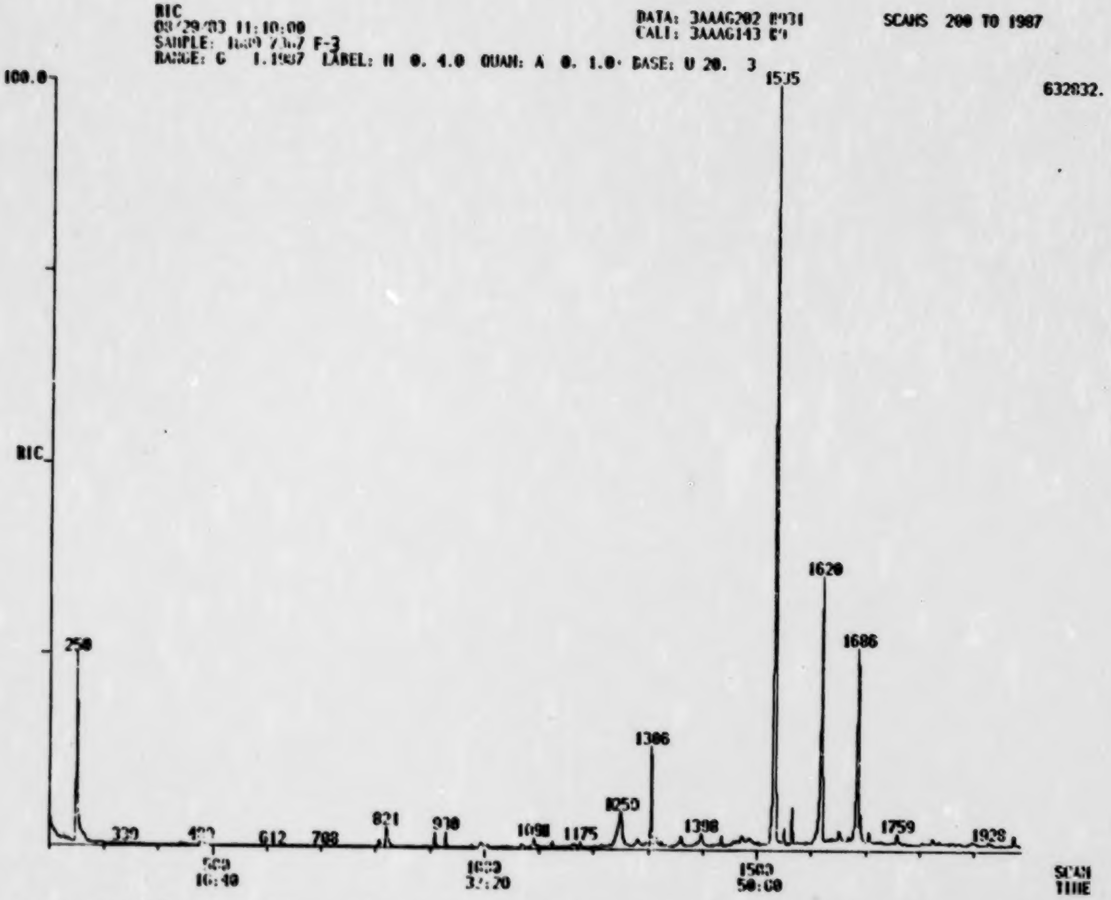


Figure 5.48. Capillary chromatogram of extract 7367 (base/neutral), fraction 3.

Table 5.4. Compounds observed in the fractions obtained from extract 7367 (base/neutral)

Compound	Scan	Fit
Fraction 1		
octadecane	961	941
pentacosane	1049	936
2,6,10,15-tetramethylheptadecane	1128	923
hexatriacontane	1201	952
hexatriacontane	1276	942
Fraction 2		
3-methyl-2-cyclohexen-1-one	278	948
d_8-naphthalene	452	-
d_{10}-anthracene	1075	-
octadecanal	1127	874
octahydro-1-(2-octyldecyl)pentalene	1327	893
Fraction 3		
5-ethyl-2-heptanol	808	907
2-(2-phenoxyethoxy)ethanol	821	906
4-butoxy-1-butanol	909	809
2-methylhexanoic acid	1250	860
bis(2-ethylhexyl)nonanedioate	1535	805
dioctyl phthalate	1620	808
octadecanol	1686	857

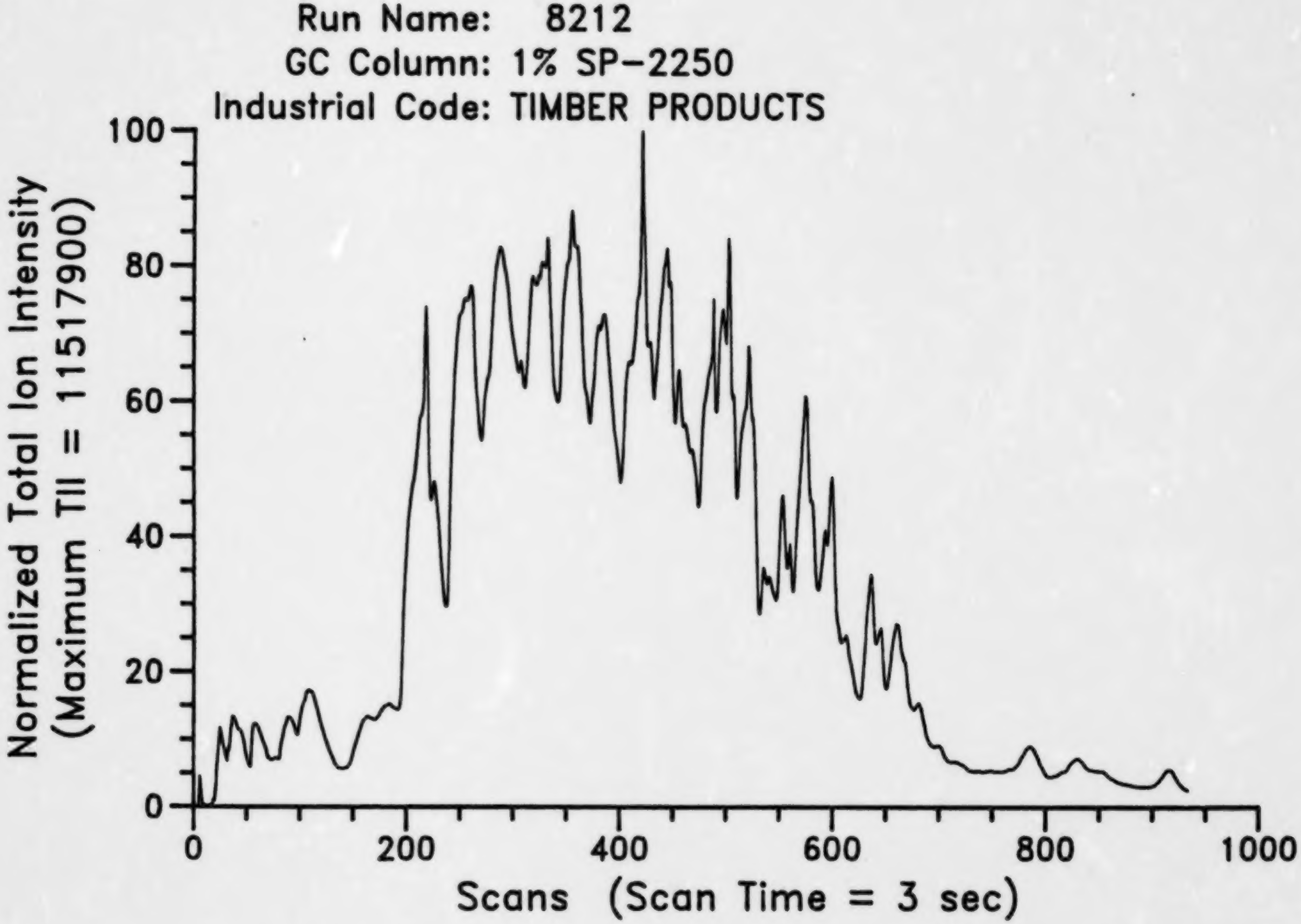


Figure 5.49. Packed column chromatogram, extract 8212 (base/neutral), timber products industry.

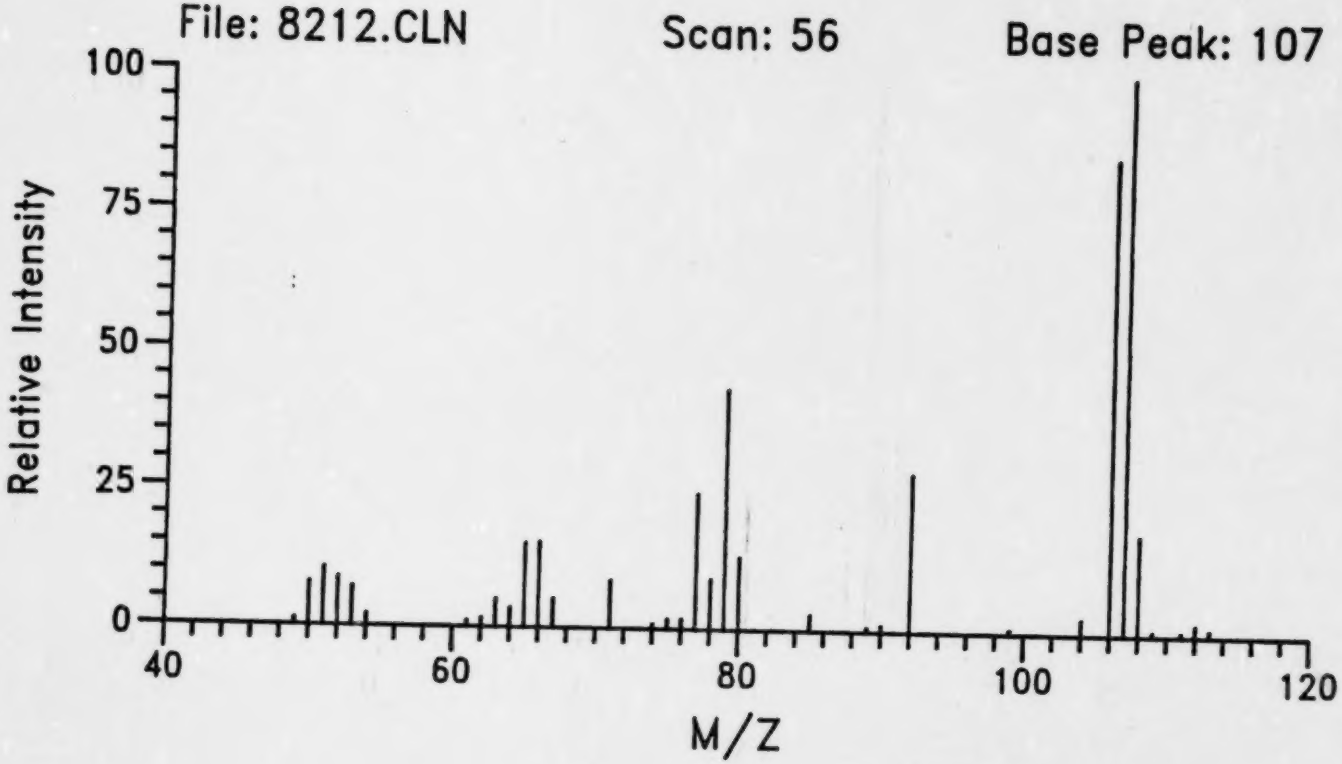


Figure 5.50. Extract 8212 (base/neutral), timber products industry. Frequency of occurrence: 5.

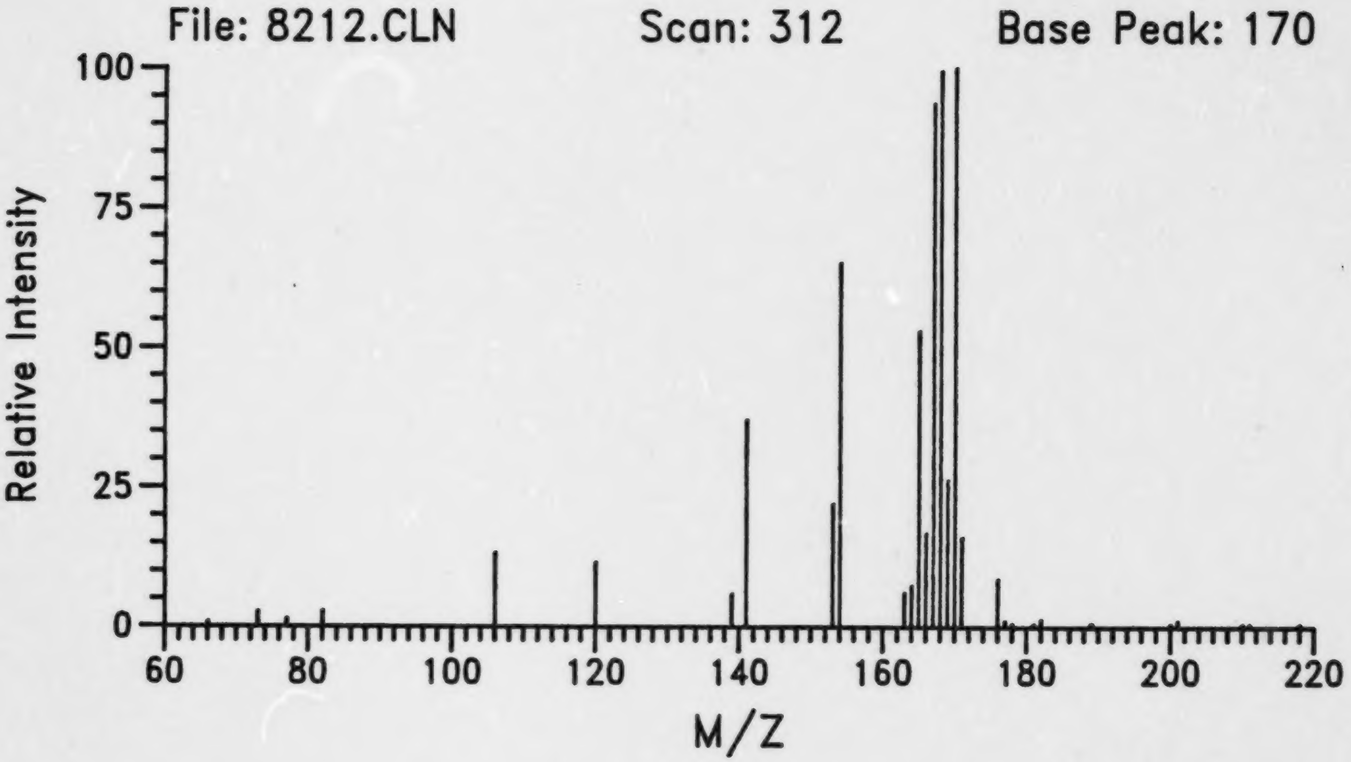


Figure 5.51. Extract 8212 (base/neutral), timber products industry. Frequency of occurrence: 6.

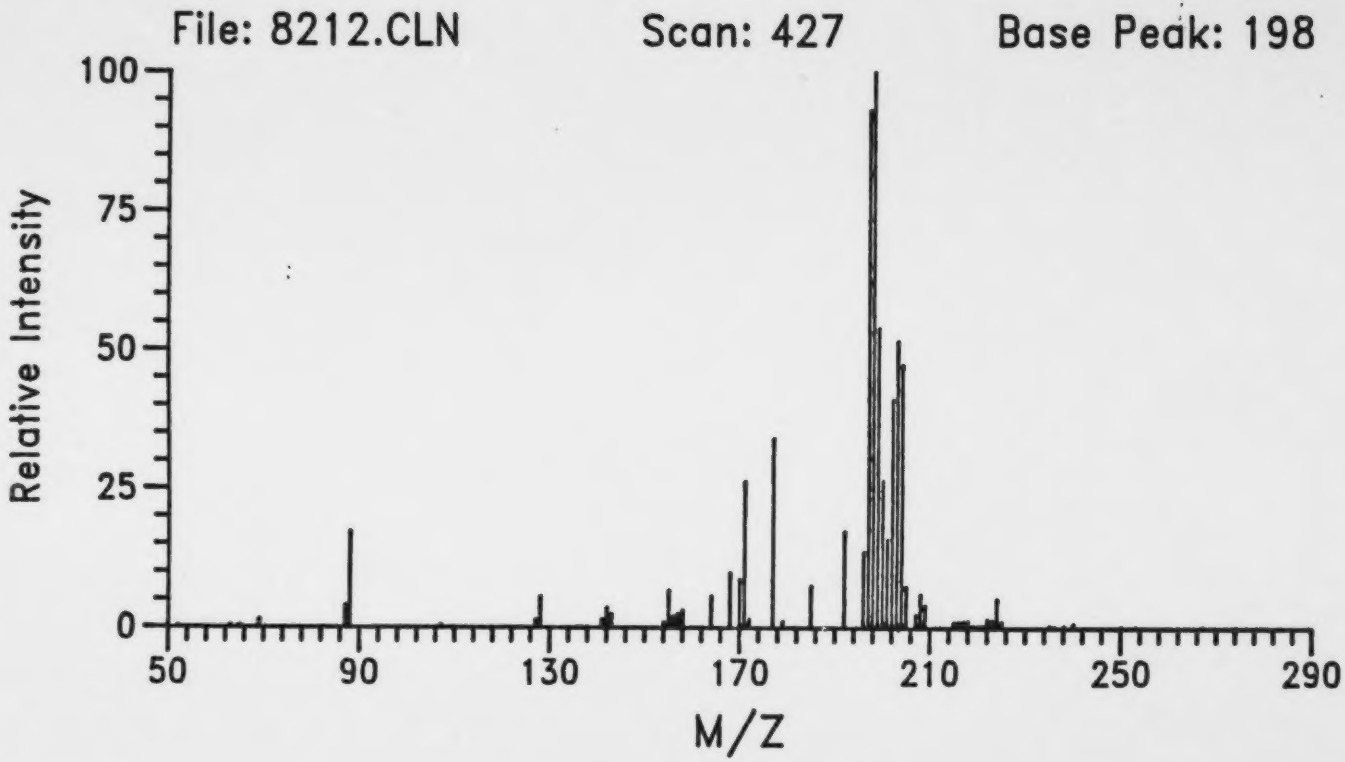


Figure 5.52. Extract 8212 (base/neutral), timber products industry. Frequency of occurrence: 7.

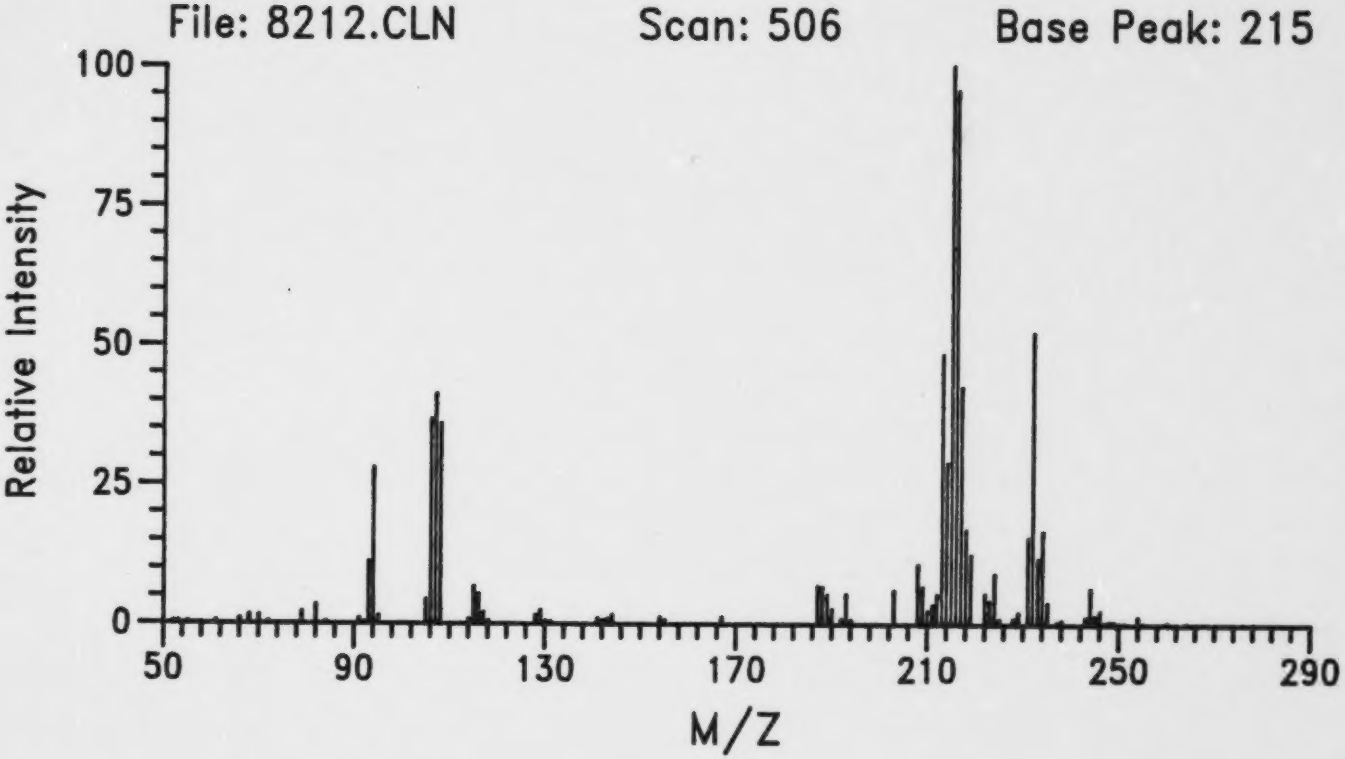


Figure 5.53. Extract 8212 (base/neutral), timber products industry. Frequency of occurrence: 7.

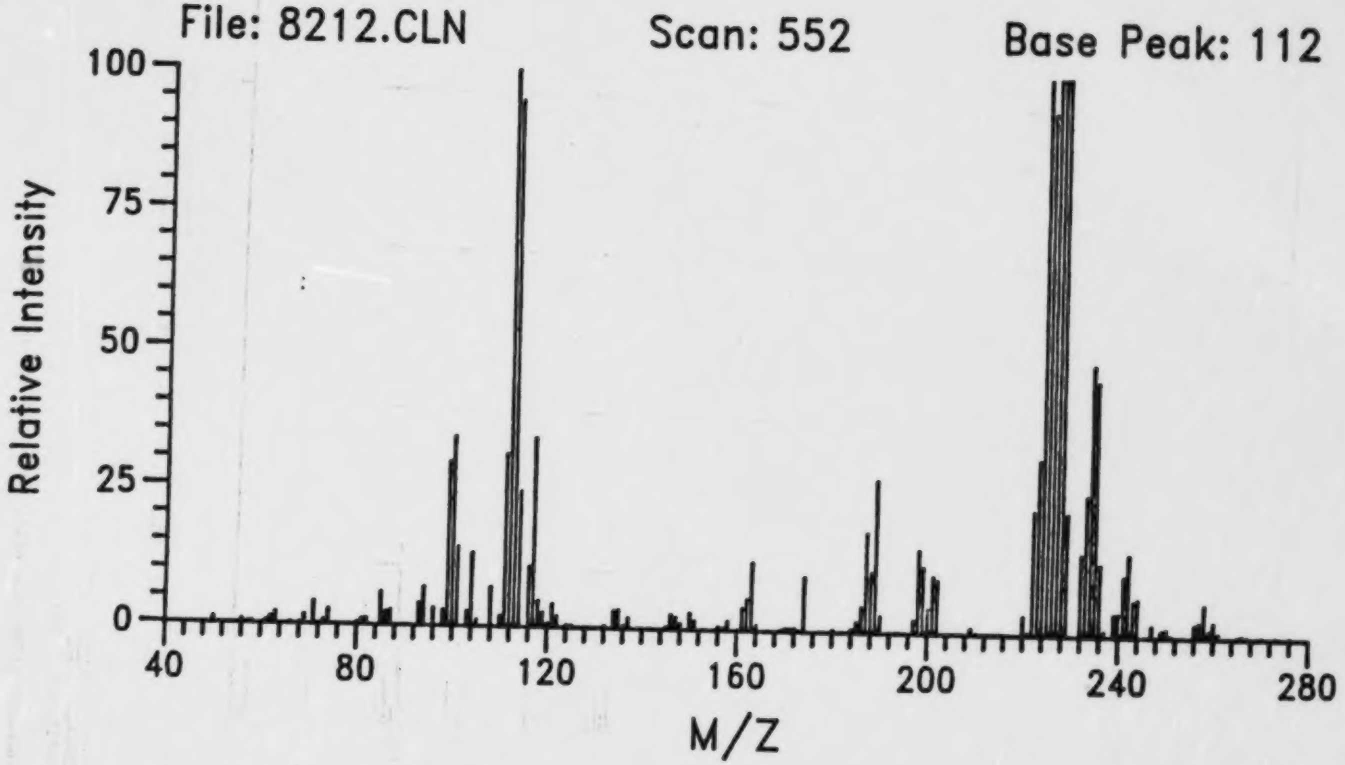


Figure 5.54. Extract 8212 (base/neutral), timber products industry. Frequency of occurrence: 5.

```
RUN IDENTIFICATION 1889 R6212 (B/N) EPA*320037
SPECTRA FILE NAME AAC360
FILE POSITION    264
BACKGROUND    263
MAXIMUM INTENSITY    748          % OF TOTAL ION    35.6
OUTPUT MASS RANGE    40  TO    492
SCAN SPEED    2
MASS        198   197   199   75   81   82   116   57   186   171
INTENSITY   10000 3848  1417  989  561  534  534   481  427   401
```

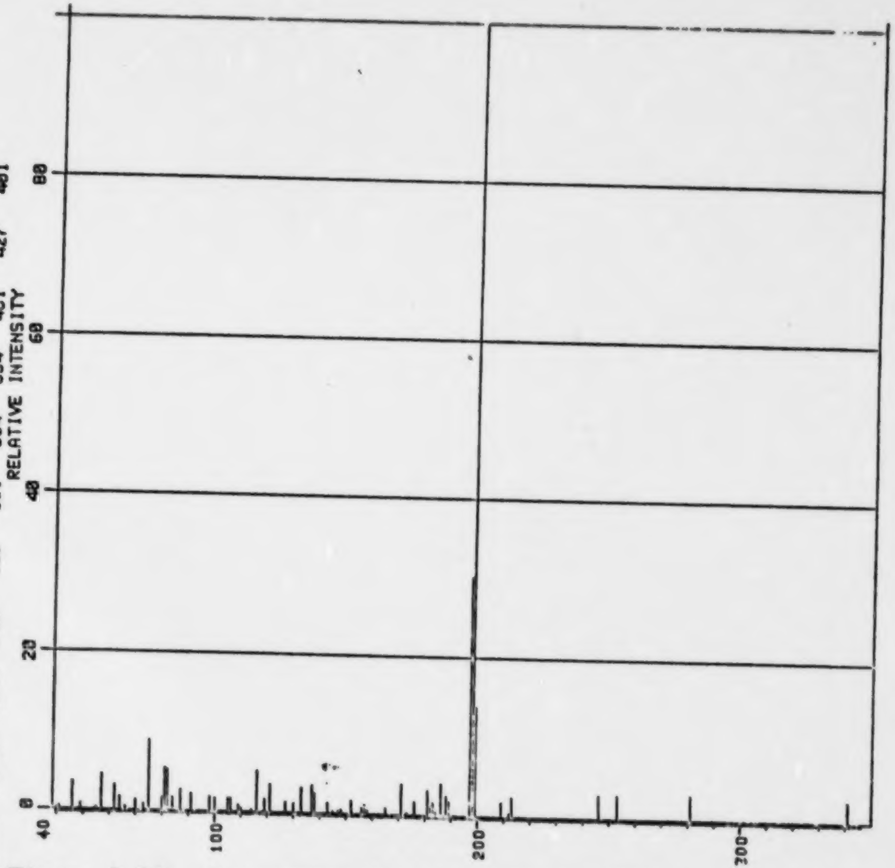


Figure 5.55. Deconvoluted mass spectrum, EPA compound of interest, molecular weight 198, scan #264.

```
RUN IDENTIFICATION 1889 RE212 (B/N) EPA*320837
SPECTRA FILE NAME ARC380
FILE POSITION    263
BACKGROUND    259
MAXIMUM INTENSITY    650        % OF TOTAL ION    12.8
OUTPUT MASS RANGE      40 TO    492
SCAN SPEED      2
MASS          204   203   202   101   196   192   201   205    88    51
INTENSITY   16780  9015  6461  2276  2215  2030  1846  1784  1661  1630
```

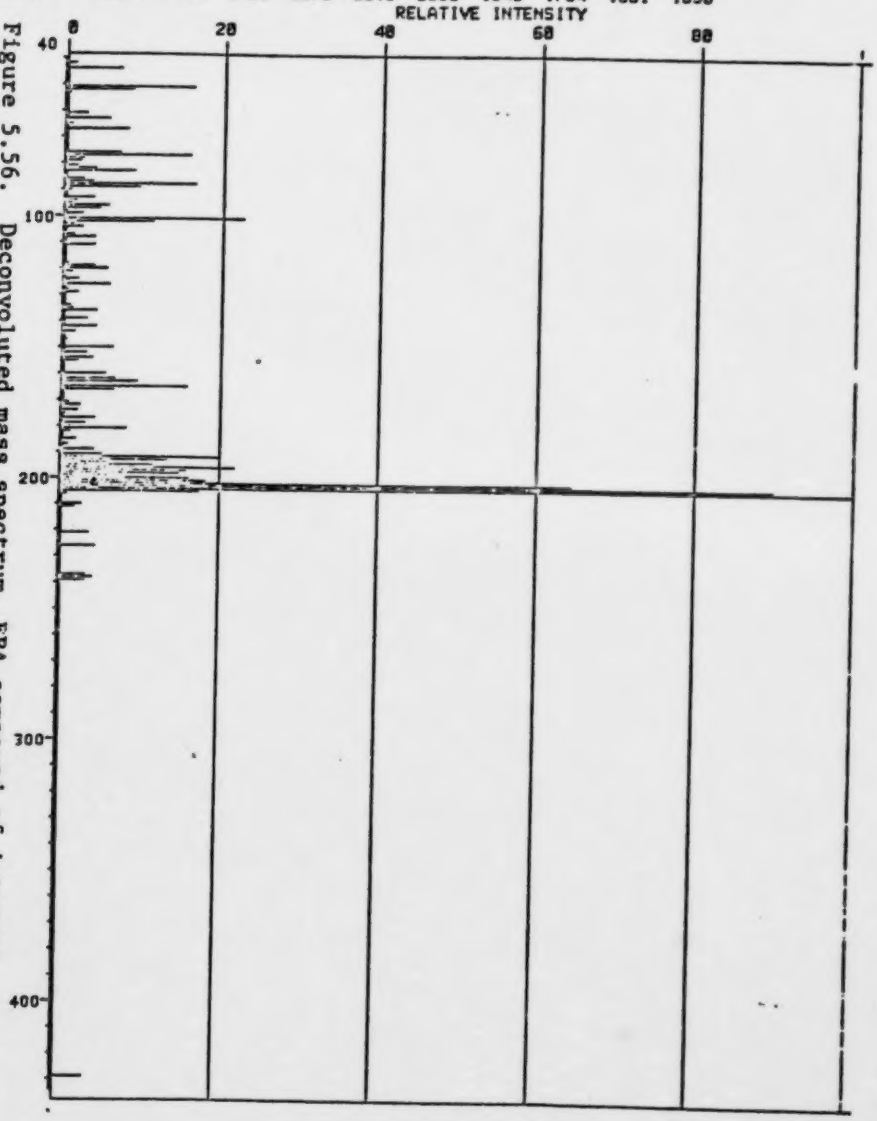


Figure 5.56. Deconvoluted mass spectrum, EPA compound of interest, molecular weight 204, scan #263.

are other possibilities which contain oxygen and nitrogen which cannot be excluded from consideration. Spectrum #506 also represents a composite mass spectrum: m/z 216 can be tentatively identified as a methylpyrene isomer, and several are present; accurate mass measurements are consistent with this identification but do not exclude other possibilities. Scan #552 (Figure 5.53) is a saturated spectrum. A corresponding spectrum is shown in Figure 5.57, and the compound is tentatively identified as benzo[ghi]fluoranthene, a finding consistent with the accurate mass measurements. The chromatogram was extremely complex, over a high background of hydrocarbons; even with the resolution attainable on a 60 m capillary column, many of the multiple-component mass spectra could not be deconvoluted. A laboratory cleanup procedure was therefore executed, and the resulting fractions analyzed. Fraction 1 (Figure 5.58) shows a clean chromatogram with peaks at nearly baseline chromatographic resolution. Several of the components of interest are to be found in this fraction. A typical spectrum of a trialkylnaphthalene is shown in Figure 5.59, the extracted ion current profile for the family of compounds in Figure 5.60. A representative output of a library search is shown in Figure 5.61. The mass spectra of the compounds of interest are cleaner in the purified fraction. At least 10-11 members of the class of trialkylnaphthalenes appear to be present in this fraction. It is also possible to observe the convoluted mass spectrum which contains m/z 198 and 204 (see Figure 5.62), and an extracted ion current profile of m/z 198 (Figure 5.63) again shows that several members of a family appear to be present. The library search of one of the members of this family (Figure 5.64) identifies this compound as a methyldibenzothiophene. A clean mass spectrum of this compound is shown in Figure 5.65. The extracted ion current profile in Figure 5.63 also shows m/z 215 and demonstrates that several members of this family are to be found in this fraction. Identifications made by the library search (Figure 5.66) include benzofluorene and methylpyrene, both $C_{17}H_{12}$ isomers. A description of compounds observed in this fraction is presented in Table 5.5.

```
RUN IDENTIFICATION 1859 K8212 (B/N) EPA•32C037
SPECTRA FILE NAME AAC380
FILE POSITION    464
BACKGROUND    479
MAXIMUM INTENSITY    752          % OF TOTAL ION    19.9
OUTPUT MASS RANGE    43  TO    432
SCAN SPEED    2
MASS          226   228   227   113   224   112   225    57    74   223
INTENSITY   10000  5478  3111  2645  2180  2154  1861  1569   824   771
```

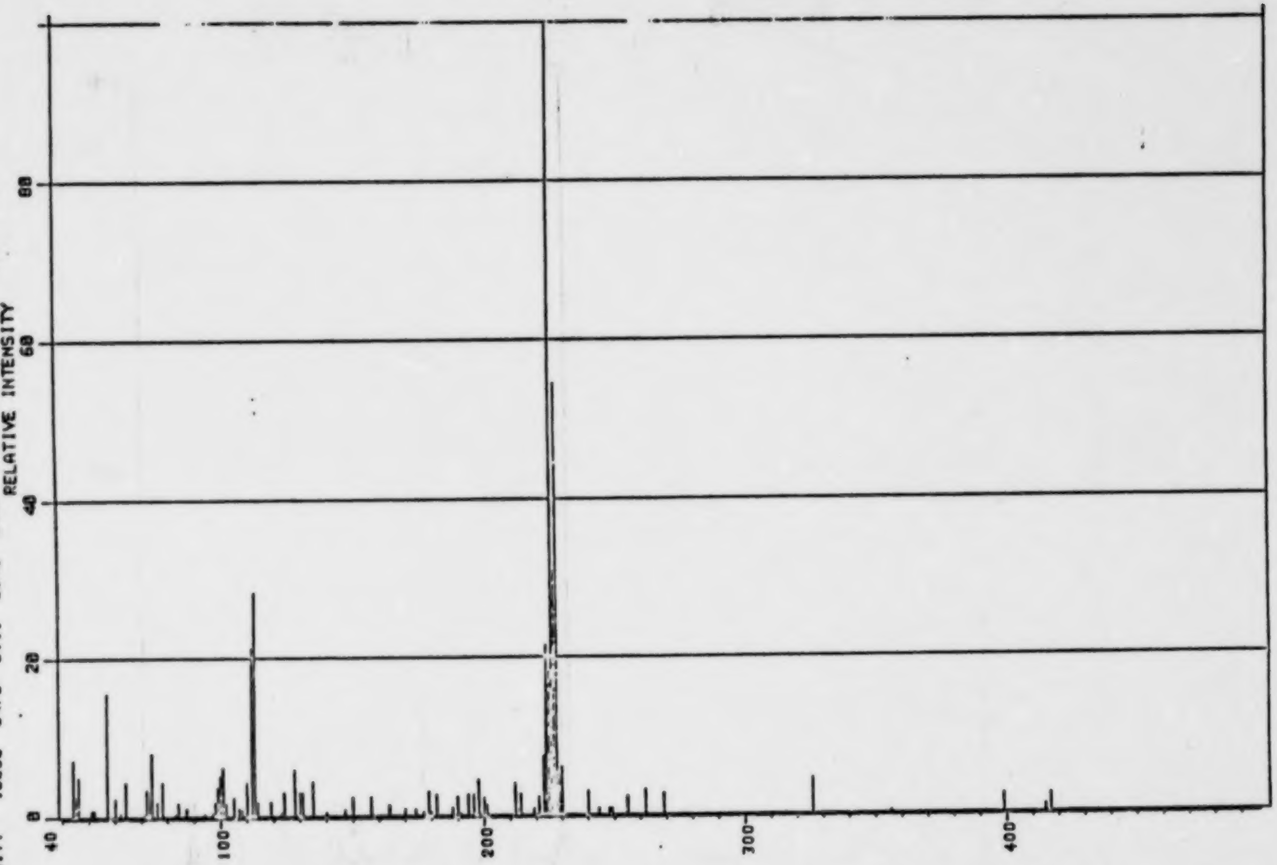


Figure 5.57. Mass spectrum of EPA compound of interest, tentatively identified as benzo[ghi]fluoranthene, scan #484.

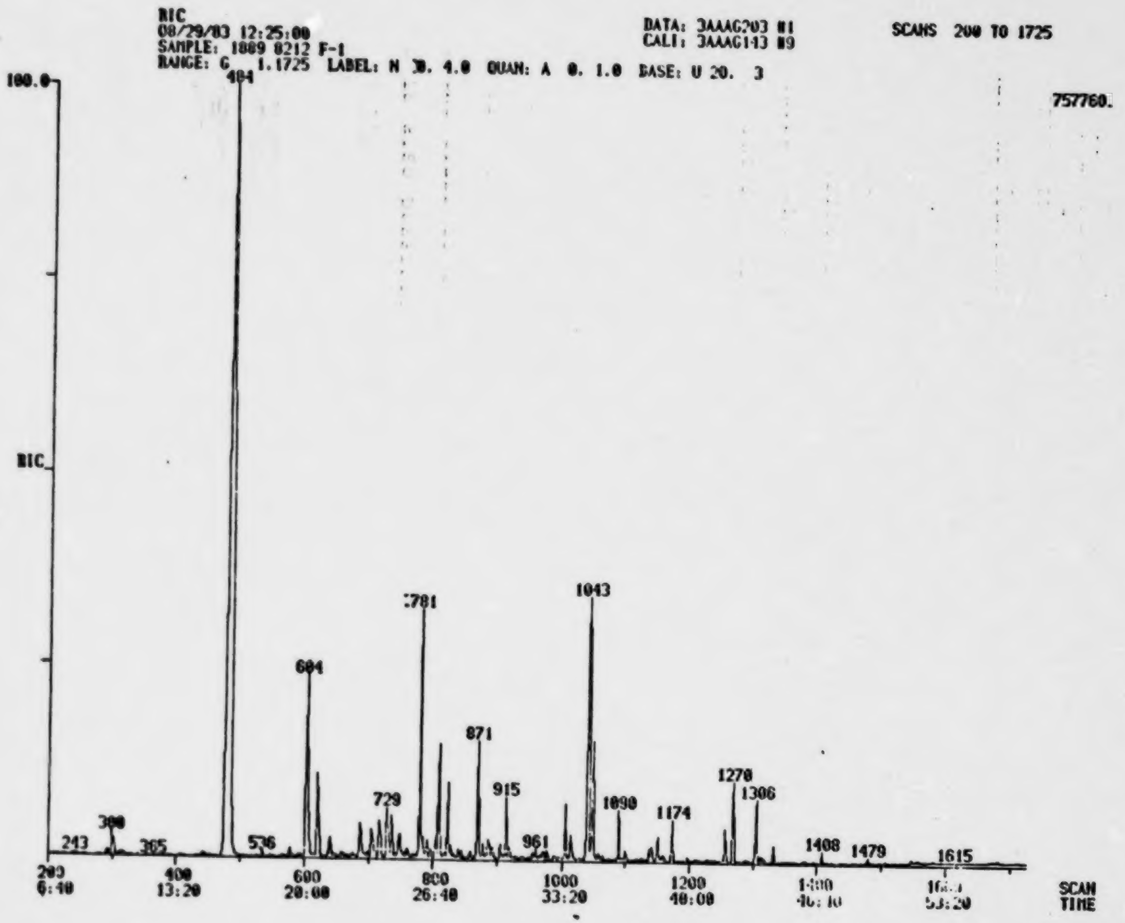


Figure 5.58. Capillary chromatogram of extract 8212 (base/neutral), fraction 1.

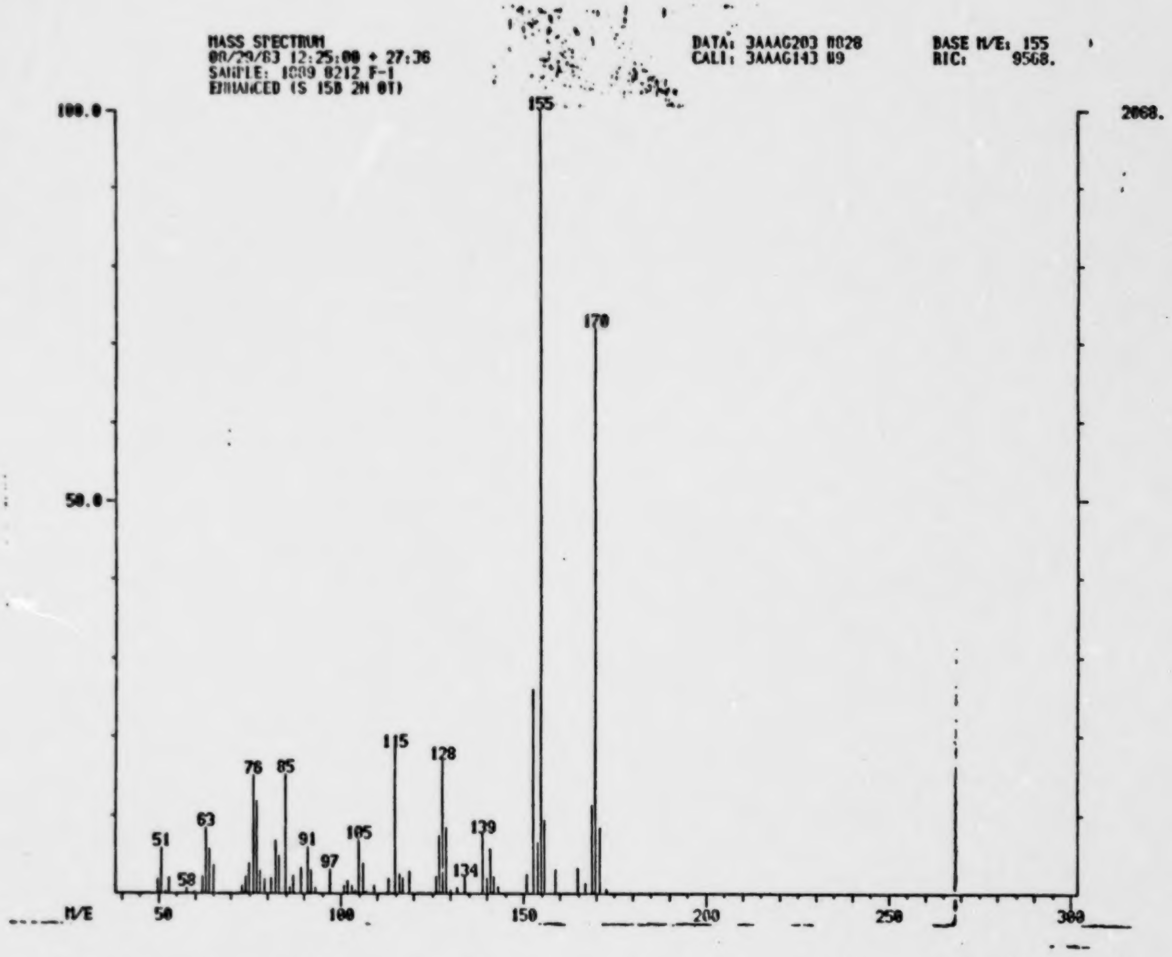


Figure 5.59. Mass spectrum of a component of interest (deconvoluted by extract fractionation), tentatively identified as a trialkylnaphthalene, scan #828.

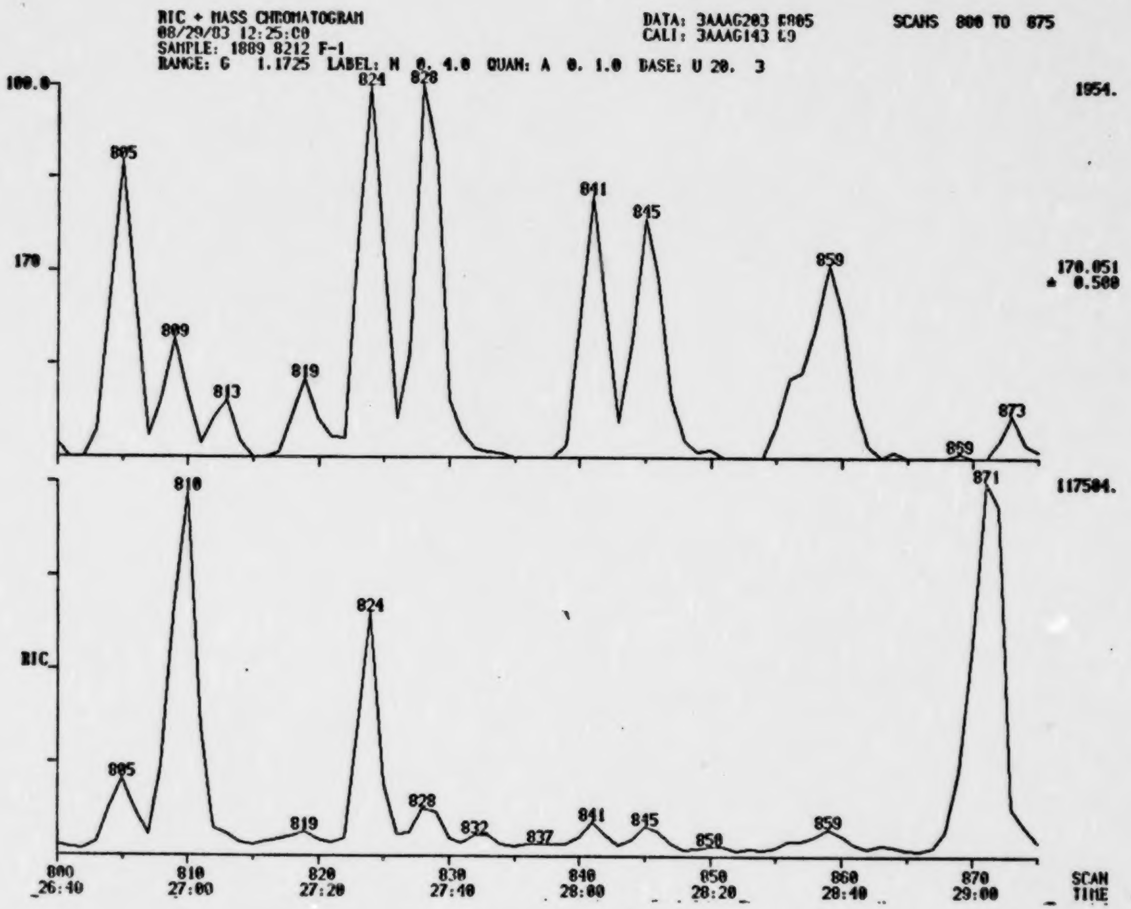


Figure 5.60. Extracted ion current profile, m/z 170, extract 8212 (base/neutral), fraction 1.

Figure 5.61. Library search, trialkylnaphthalene, extract 8212 (base/neutral), fraction 1.

```
LIBRARY SEARCH                      DATA: 3AAAG203 * 859      BASE M/E:  155
08/29/83 12:25:00 + 28:38           CALI: 3AAAG143 *   9      RIC:      6927.
SAMPLE: 1889 8212 F-1
ENHANCED (S 15B 2N 0T)

25499 SPECTRA IN LIBRARYNB SEARCHED FOR MAXIMUM PURITY
   54 MATCHED AT LEAST 6 OF THE 16 LARGEST PEAKS IN THE UNKNOWN
   54 PASSED IFORM.TEST;C: 0-63,O: 0-15,N: 0-15,S: 0-15,CL: 0-15,XX: 0-99

RANK IN NAME
1   4193 NAPHTHALENE,2,3,6-TRIMETHYL-
2   6108 NAPHTHALENE,1,6,7-TRIMETHYL-
3   5822 NAPHTHALENE,2-(1-METHYLETHYL)-
4  15263 NAPHTHALENE,(1-METHYLETHYL)-
5   6819 NAPHTHALENE,1,3,6-TRIMETHYL-

RANK  FORMULA                            M.WT B.PK   PURITY   FIT   RFIT
1 C13.H14                                 170  170      767   909    805
2 C13.H14                                 170  170      759   908    801
3 C13.H14                                 170  155      735   914    775
4 C13.H14                                 170  155      711   890    761
5 C13.H14                                 170  170      643   946    643
```

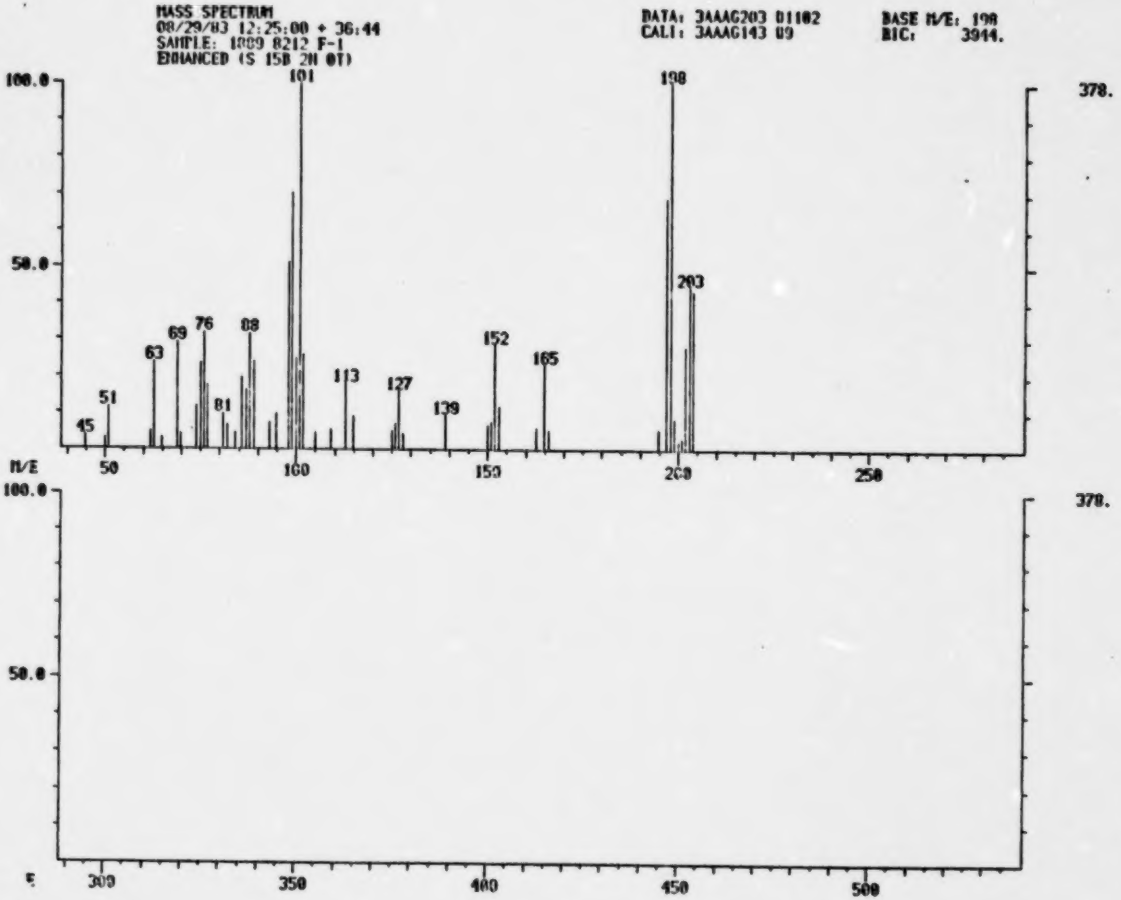


Figure 5.62. Convoluted mass spectrum (extract 8212 (base/neutral)), fraction 1 showing m/z 198 and 204.

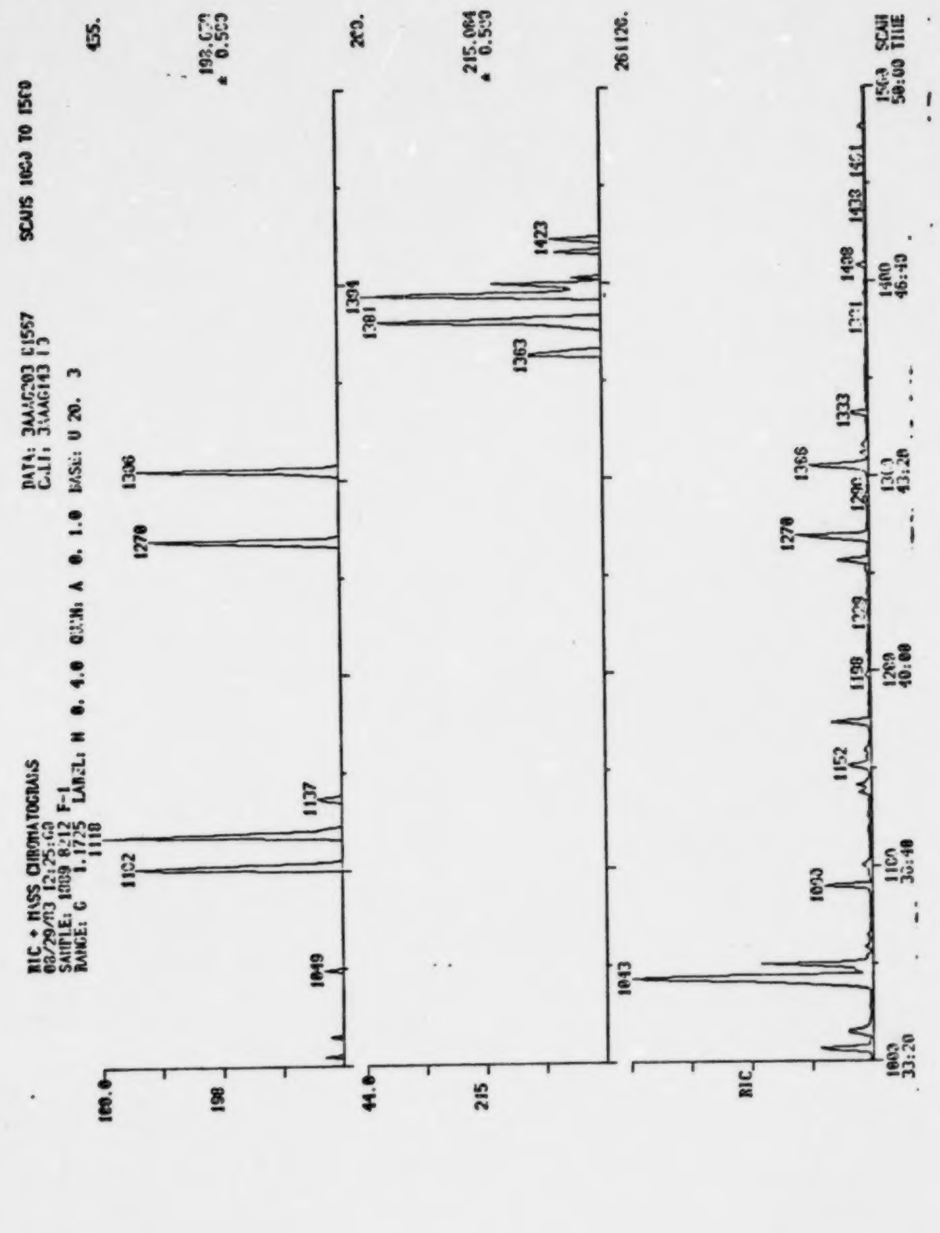


Figure 5.63. Extracted ion current profile, m/z 198 and 215.

Figure 5.64. Library search, scan #1118, base peak m/z 198.

```
LIBRARY SEARCH                  DATA: 3AAAG203 #1118      BASE M/E:  198
08/29/83 12:25:00 + 37:16       CALI: 3AAAG143 #   9      RIC:       1279.
SAMPLE: 1889 8212 F-1
ENHANCED (S 15B 2N CT)

25499 SPECTRA IN LIBRARYNB SEARCHED FOR MAXIMUM PURITY
  133 MATCHED AT LEAST 4 OF THE 16 LARGEST PEAKS IN THE UNKNOWN
  133 PASSED !FORM.TEST;C: 0-63,O: 0-15,N: 0-15,S: 0-15,CL: 0-15,XX: 0-99

RANK IN NAME
1 11565 DIBENZOTHIOPHENE,3-METHYL-
2  9555 DIBENZOTHIOPHENE,4-METHYL-
3  1882 9H-THIOXANTHENE
4  3957 BENZENE,1-FLUORO-4-(2-PHENYLETHENYL)-,(E)-
5  6826 BENZENE,1-FLUORO-3-(2-PHENYLETHENYL)-,(E)-

RANK  FORMULA                                  M.WT B.PK   PURITY    FIT   RFIT
1 C13.H10.S                                     198  198      701    815    807
2 C13.H10.S                                     198  198      679    813    782
3 C13.H10.S                                     198  197      569    713    614
4 C14.H11.F                                     198  198      541    732    659
5 C14.H11.F                                     198  198      537    704    701
```

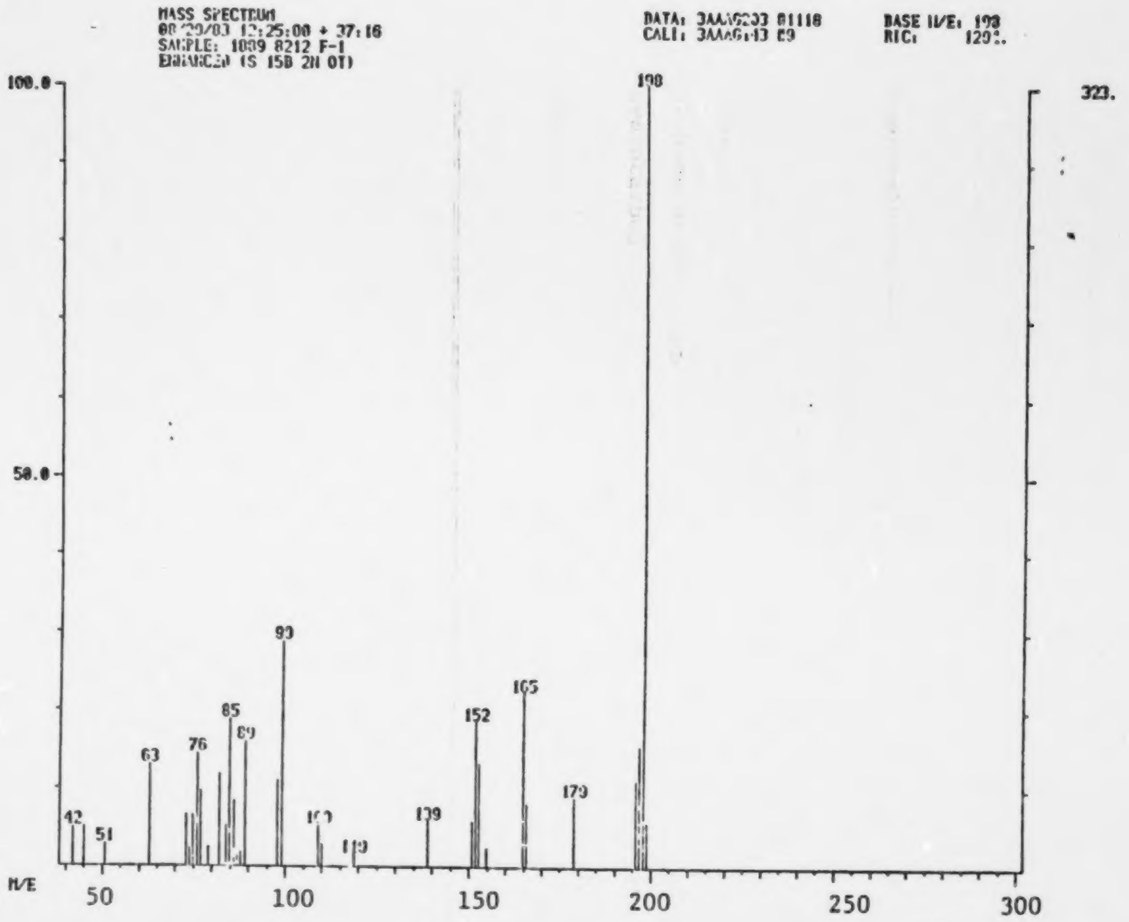
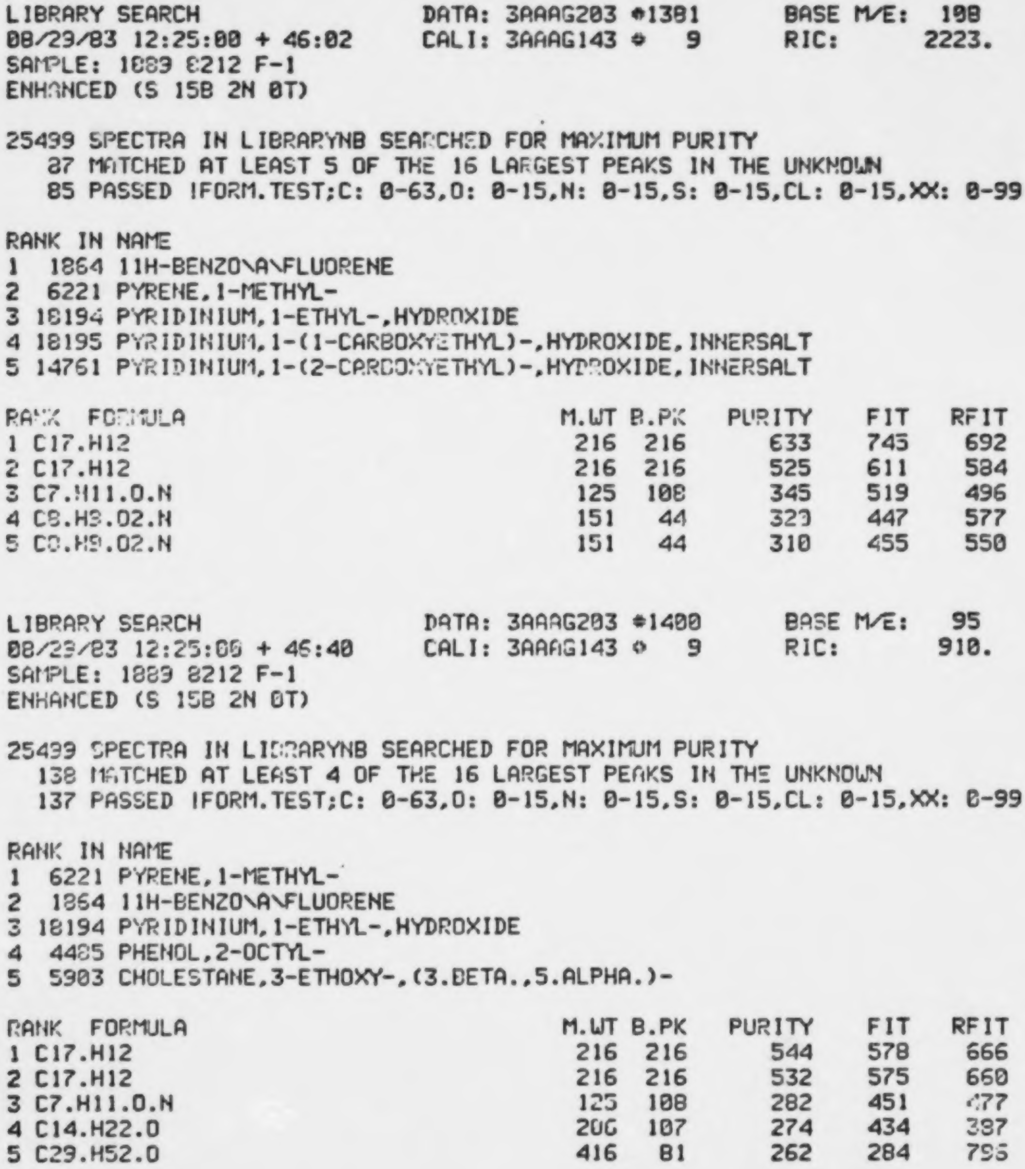


Figure 5.65. Mass spectrum of a compound identified as a methyldibenzothiophene isomer.

Figure 5.66. Library search, spectra containing ions at mass 215/216.



```
LIBRARY SEARCH                 DATA: 3AAAG203 #1381       BASE M/E:  108
08/29/83 12:25:00 + 46:02      CALI: 3AAAG143 #   9       RIC:        2223.
SAMPLE: 1889 8212 F-1
ENHANCED (S 15B 2N 0T)

25499 SPECTRA IN LIBRARYNB SEARCHED FOR MAXIMUM PURITY
   87 MATCHED AT LEAST 5 OF THE 16 LARGEST PEAKS IN THE UNKNOWN
   85 PASSED !FORM.TEST;C: 0-63,O: 0-15,N: 0-15,S: 0-15,CL: 0-15,XX: 0-99

RANK IN NAME
1   1864 11H-BENZO\A\FLUORENE
2   6221 PYRENE,1-METHYL-
3  18194 PYRIDINIUM,1-ETHYL-,HYDROXIDE
4  18195 PYRIDINIUM,1-(1-CARBOXYETHYL)-,HYDROXIDE,INNERSALT
5  14761 PYRIDINIUM,1-(2-CARBOXYETHYL)-,HYDROXIDE,INNERSALT

RANK  FORMULA                                  M.WT B.PK   PURITY    FIT   RFIT
1 C17.H12                                       216  216      633    745    692
2 C17.H12                                       216  216      525    611    584
3 C7.H11.O.N                                    125  108      345    519    496
4 C8.H9.O2.N                                    151   44      329    447    577
5 C8.H9.O2.N                                    151   44      310    455    550

LIBRARY SEARCH                 DATA: 3AAAG203 #1400       BASE M/E:   95
08/29/83 12:25:00 + 46:40      CALI: 3AAAG143 #   9       RIC:         910.
SAMPLE: 1889 8212 F-1
ENHANCED (S 15B 2N 0T)

25499 SPECTRA IN LIBRARYNB SEARCHED FOR MAXIMUM PURITY
  138 MATCHED AT LEAST 4 OF THE 16 LARGEST PEAKS IN THE UNKNOWN
  137 PASSED !FORM.TEST;C: 0-63,O: 0-15,N: 0-15,S: 0-15,CL: 0-15,XX: 0-99

RANK IN NAME
1   6221 PYRENE,1-METHYL-
2   1864 11H-BENZO\A\FLUORENE
3  18194 PYRIDINIUM,1-ETHYL-,HYDROXIDE
4   4485 PHENOL,2-OCTYL-
5   5903 CHOLESTANE,3-ETHOXY-,(3.BETA.,5.ALPHA.)-

RANK  FORMULA                                  M.WT B.PK   PURITY    FIT   RFIT
1 C17.H12                                       216  216      544    578    666
2 C17.H12                                       216  216      532    575    660
3 C7.H11.O.N                                    125  108      282    451    477
4 C14.H22.O                                     206  107      274    434    387
5 C29.H52.O                                     416   81      262    284    795
```

Table 5.5. Compounds observed in extract 8212 (base/neutral), fraction 1

Compound	Scan	Fit
methylphenylacetylene	300	993
naphthalene	484	979
2-methylnaphthalene	604	968
1-methylnaphthalene	621	965
2-_i_-propylnaphthalene	805	875
2-methylundecane	824	913
2,3,6-trimethylnaphthalene	828	940
2,6,10,15-tetramethylheptadecane	915	930
anthracene	1050	987
eicosane	1090	940
2-phenylnaphthalene	1103	750
hydrocarbon	1174	-
hydrocarbon	1257	-
pyrene	1306	986
1-methylpyrene	1394	708

A chromatogram of fraction 2 is shown in Figure 5.67. Fraction 2 is not noticeably different in polarity from fraction 1; the methyldibenzothiophenes, trialkylnaphthalenes, and methylpyrenes are observed in this fraction as well (see Table 5.6). A chromatogram of fraction 3 is shown in Figure 5.68, and a brief tabulation of peaks observed is presented in Table 5.7. The fractionation does produce cleaner chromatograms, but as inspection of the compounds observed in fractions 1 and 2 will verify, the crosstalk between fractions of the same and similar compounds is substantial. If one desired to quantify the alkylnaphthalenes, one would have to combine data from fractions 1 and 2. This same combination would also be necessary for alkylpyrenes. The partition into any given fraction is not quantitative.

Extract 11533 (Base/Neutral), Organics and Plastics Industry, Untreated Effluent

The packed column chromatogram of extract 11533 (base/neutral) is shown in Figure 5.69. The mass spectrum of the compound of interest is presented in Figure 5.70. The capillary chromatogram of extract 11533 is shown in Figure 5.71. The mass spectrum of the compound of interest as obtained from the capillary chromatogram is shown in Figures 5.72, 5.73 and 5.74. Accurate mass measurement verifies that the ion of mass 118 has a composition of C_9H_{10}, as this is the only possibility, but 6-8 possibilities (considering the presence of oxygen and nitrogen) are presented for each of the higher mass peaks measured with no way of choosing among them. Since the peaks are observed at long retention times in a complex region of the chromatogram, fractionation of the extract was attempted. The three fractions now produce extremely clean chromatograms (Figures 5.75-5.77), but a match to the mass spectrum of the compound of interest can no longer be found in any of the fractions.

Extract 12245 (Base/Neutral), Timber Products Industry, Storm Water Runoff

The packed column chromatogram of extract 12245 (base/neutral) is shown in Figure 5.78. The mass spectrum of the compound of interest is presented in Figure 5.79. The capillary chromatogram of extract 12245 is shown in Figure 5.80. The mass spectrum of the compound of interest

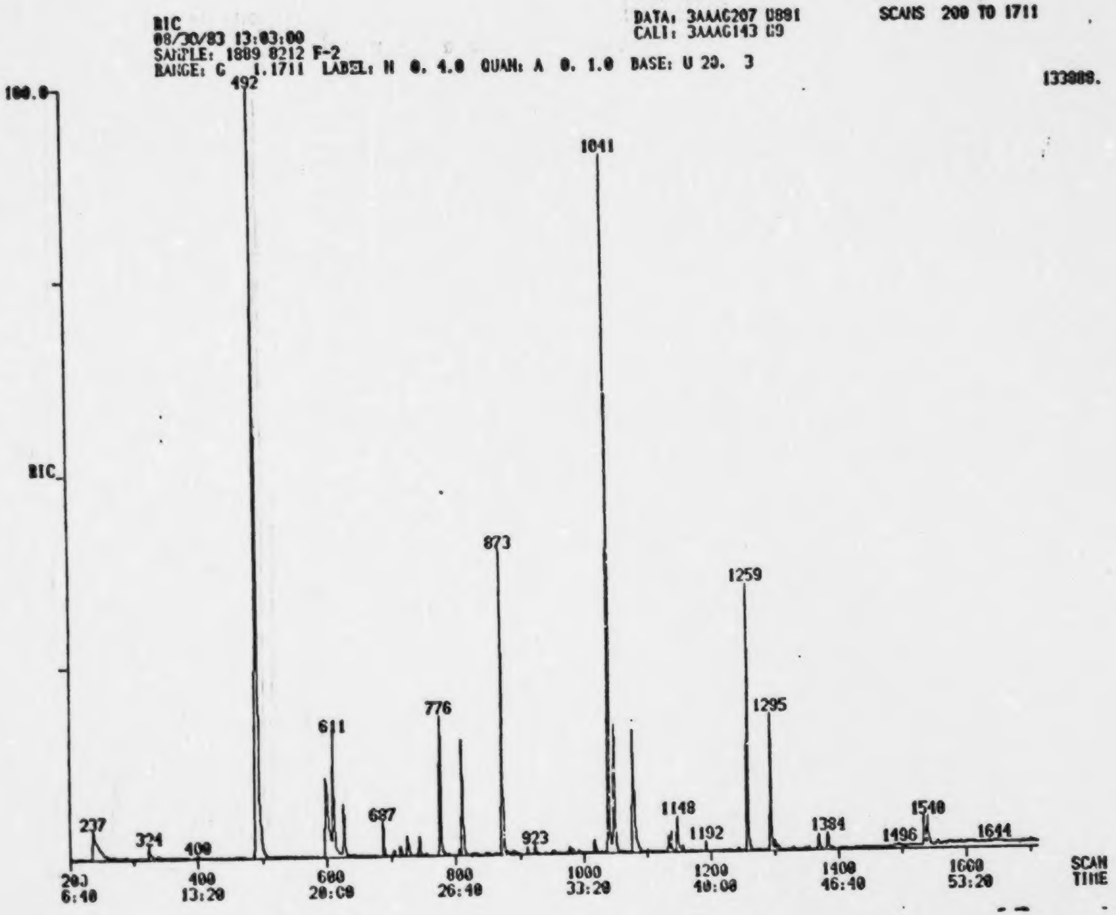


Figure 5.67. Capillary chromatogram of fraction 2, extract 8212 (base/neutral).

Table 5.6. Components of fraction 2.

Compound	Scan	Fit
benzonitrile	237	983
naphthalene	492	995
2-methylnaphthalene	627	961
dibenzofuran	811	986
1,3,6-trimethylnaphthalene	827	837
C_3-naphthalene	847	-
C_3-naphthalene	852	-
C_3-naphthalene	863	-
1-(2-propenyl)naphthalene	881	670
carbazole	1079	986
pyrene	1295	982
4-methyldibenzothiophene	1101	670
1-methylpyrene	1384	750
chrysene	1540	806

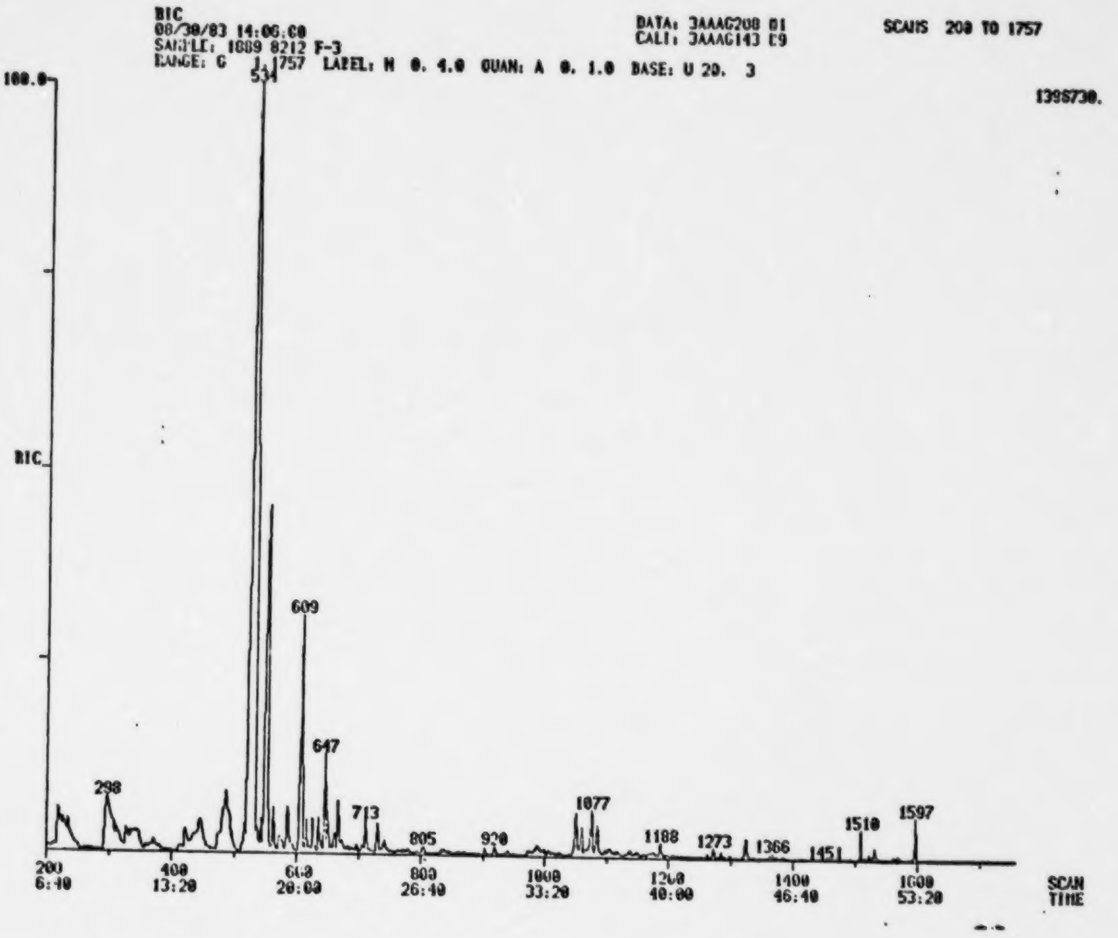


Figure 5.68. Capillary chromatogram of extract 8212 (base/neutral), fraction 3.

Table 5.7. Components of fraction 3.

Compound	Scan	Fit
isoquinoline	534	964
isoquinoline	554	995
2-methylquinoline	609	928
carbazole	920	963
benzo[H]quinoline	1077	975
9-anthracenecarbonitrile	1325	928
acridine	1052	934
benzoquinoline	1061	840
diisooctyl phthalate	1597	816

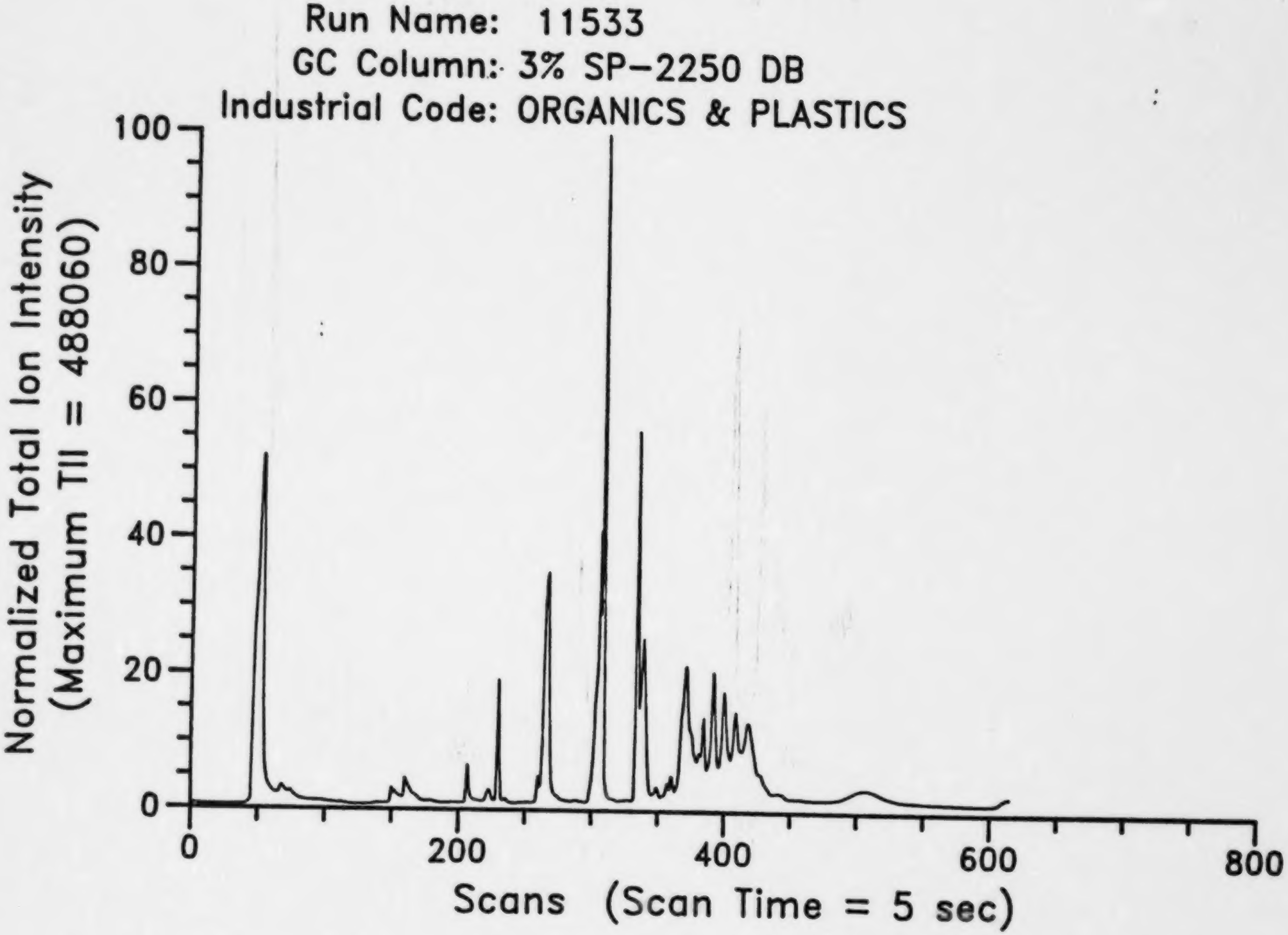


Figure 5.69. Packed column chromatogram, extract 11533 (base/neutral), organics and plastics industry.

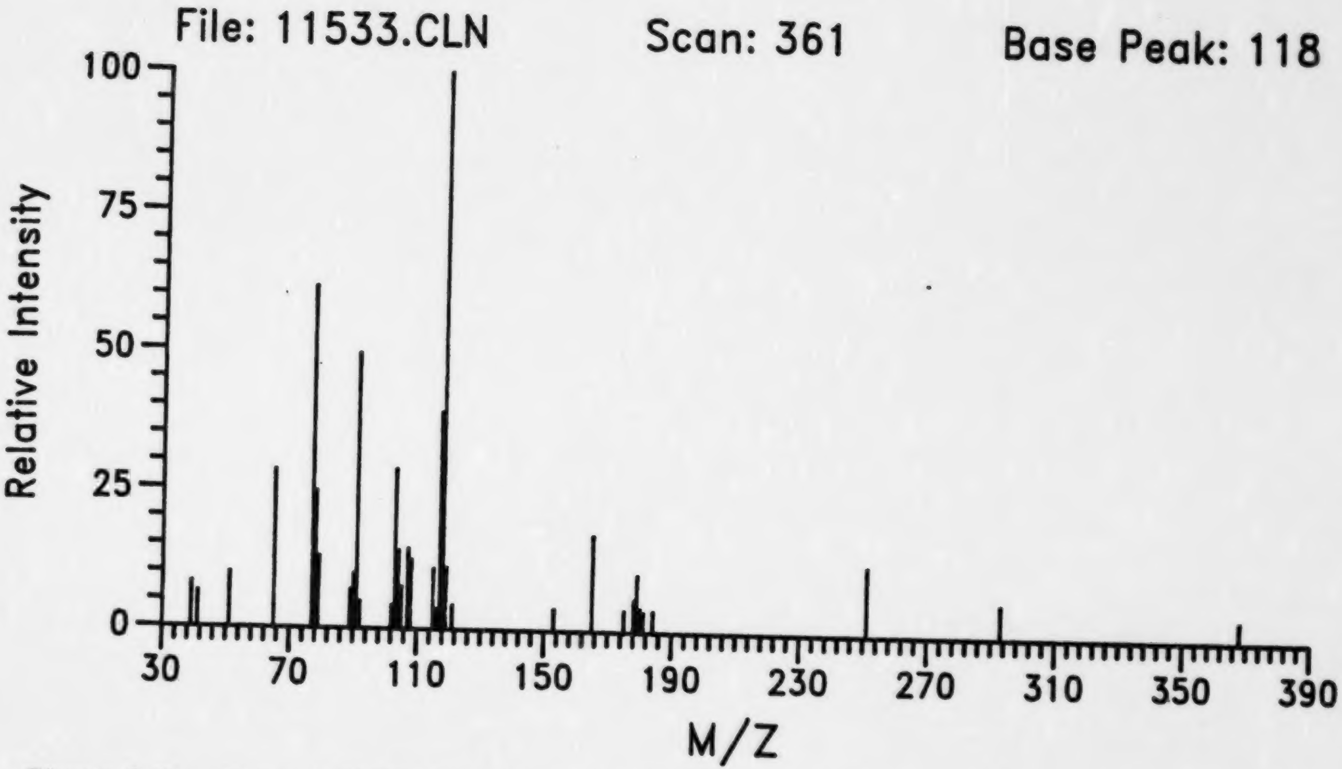


Figure 5.70. Extract 11533 (base/neutral), organics and plastics industry. Frequency of occurrence: 21.

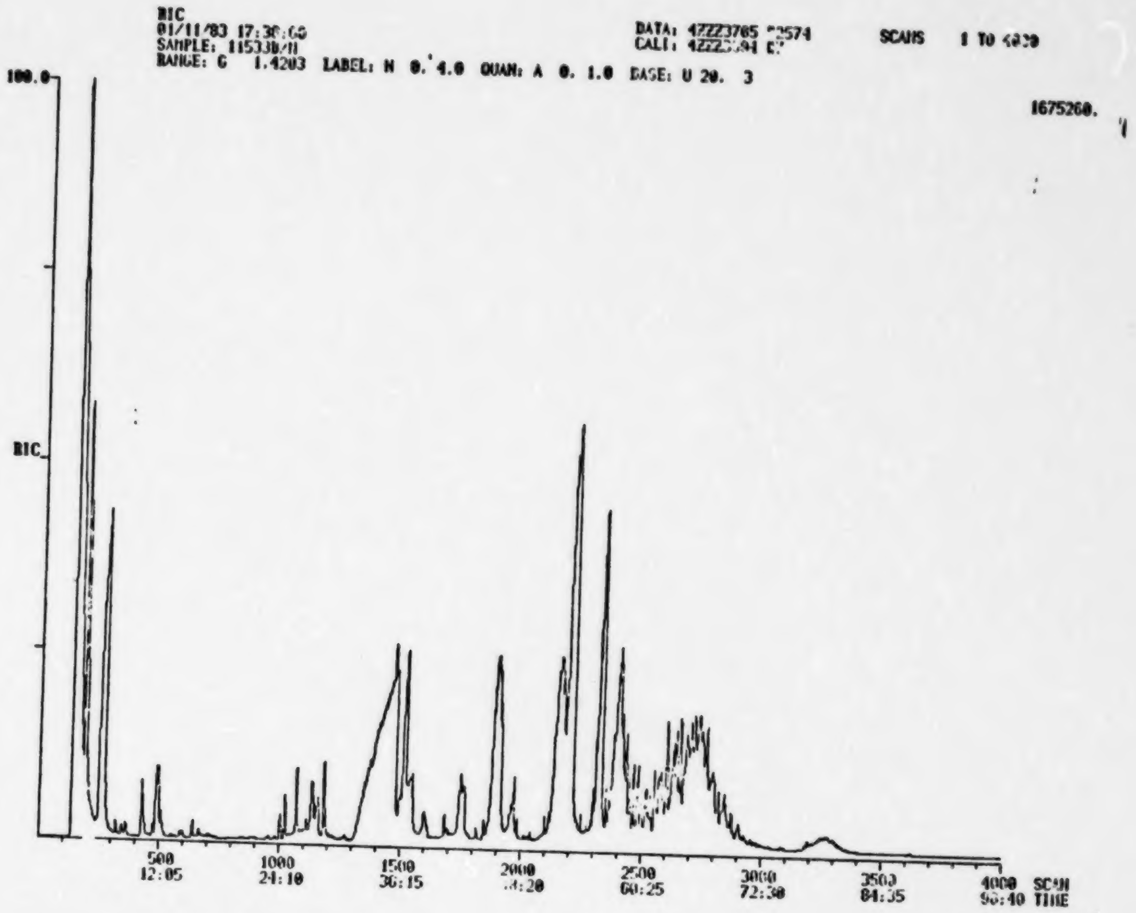


Figure 5.71. Capillary chromatogram of extract 11533 (base/neutral), organics and plastics industry.

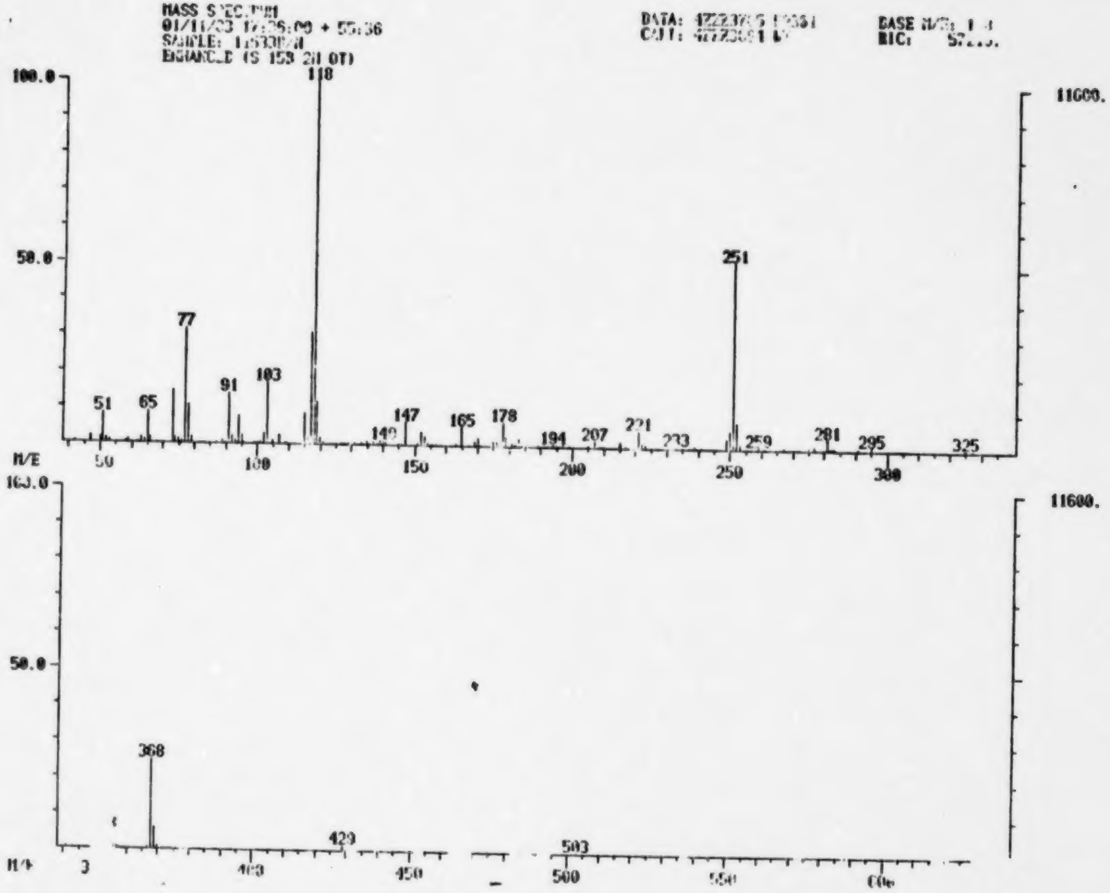


Figure 5.72. Mass spectrum of EPA compound of interest, extract 11533 (base/neutral), organics and plastics industry.

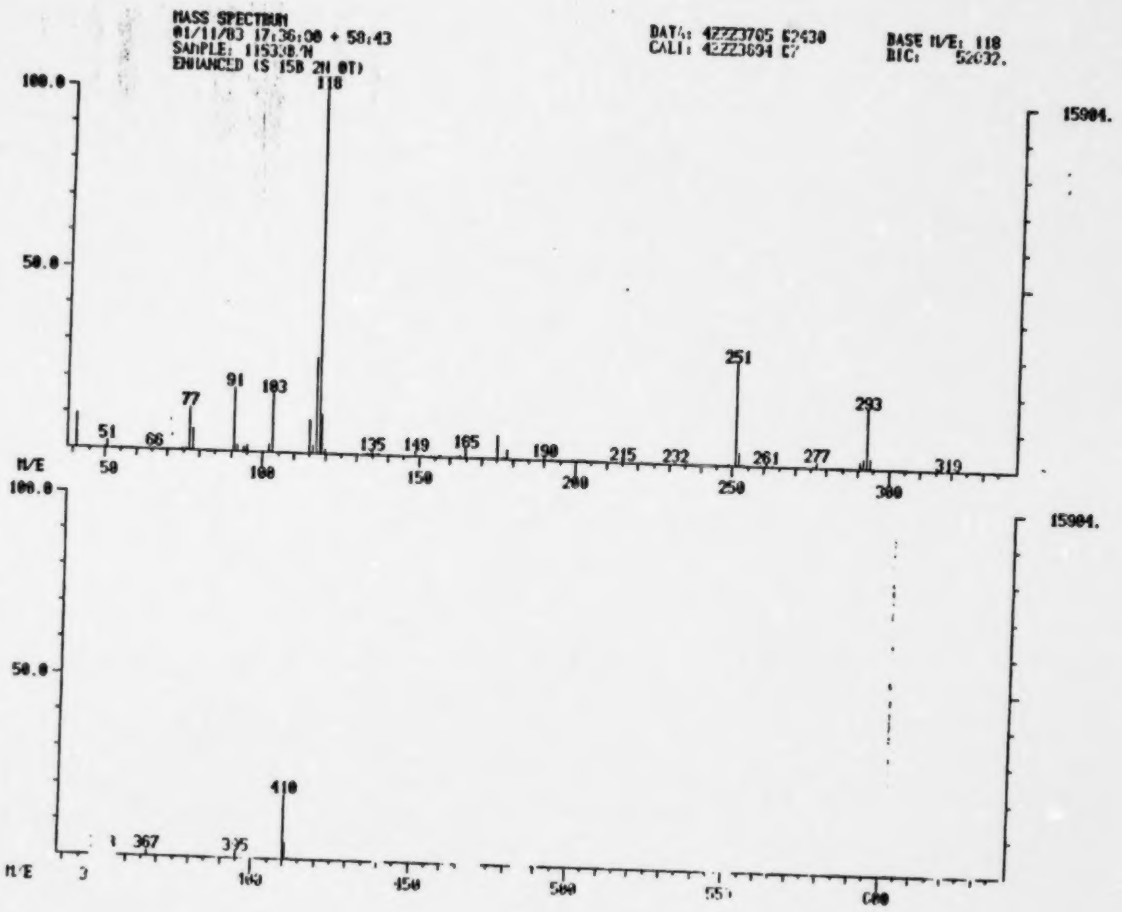


Figure 5.73. Mass spectrum of EPA compound of interest, extract 11533 (base/neutral), organics and plastics industry.

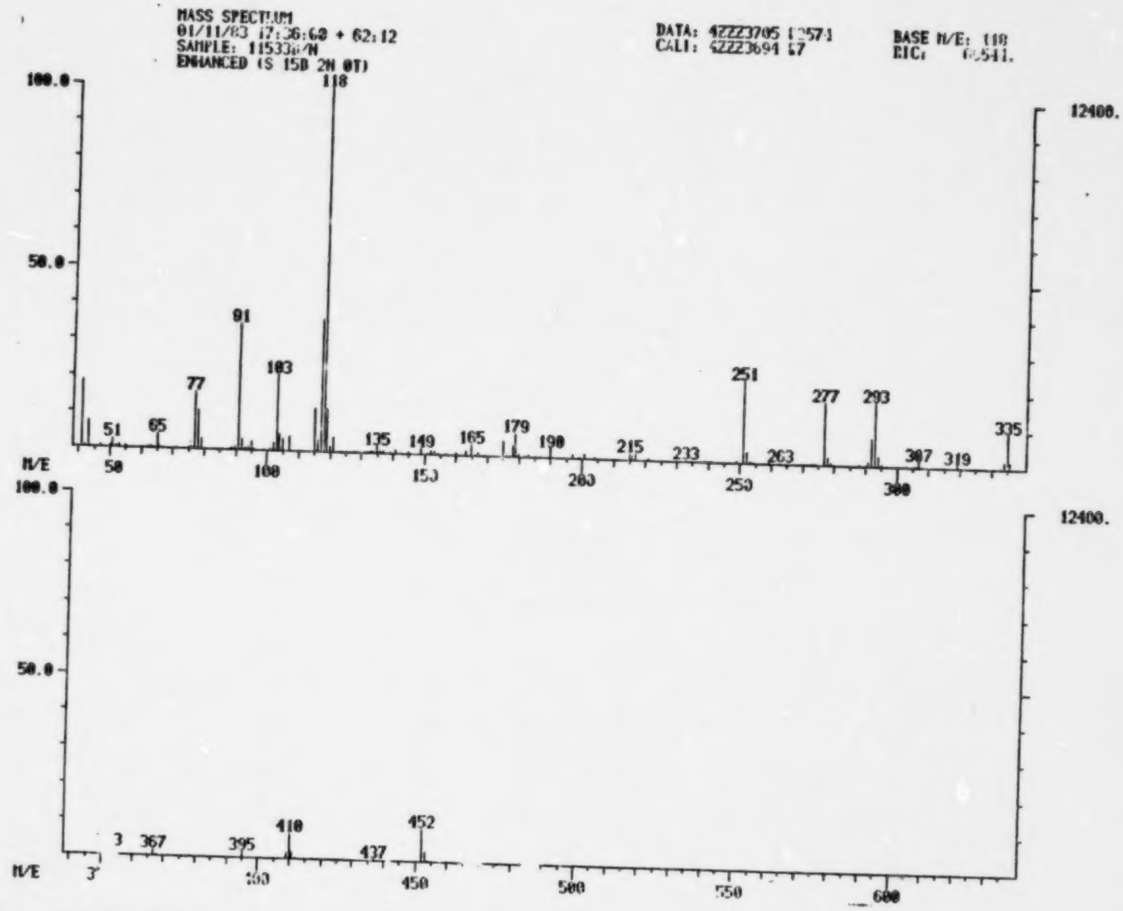


Figure 5.74. Mass spectrum of EPA compound of interest, extract 11533 (base/neutral), organics and plastics industry.

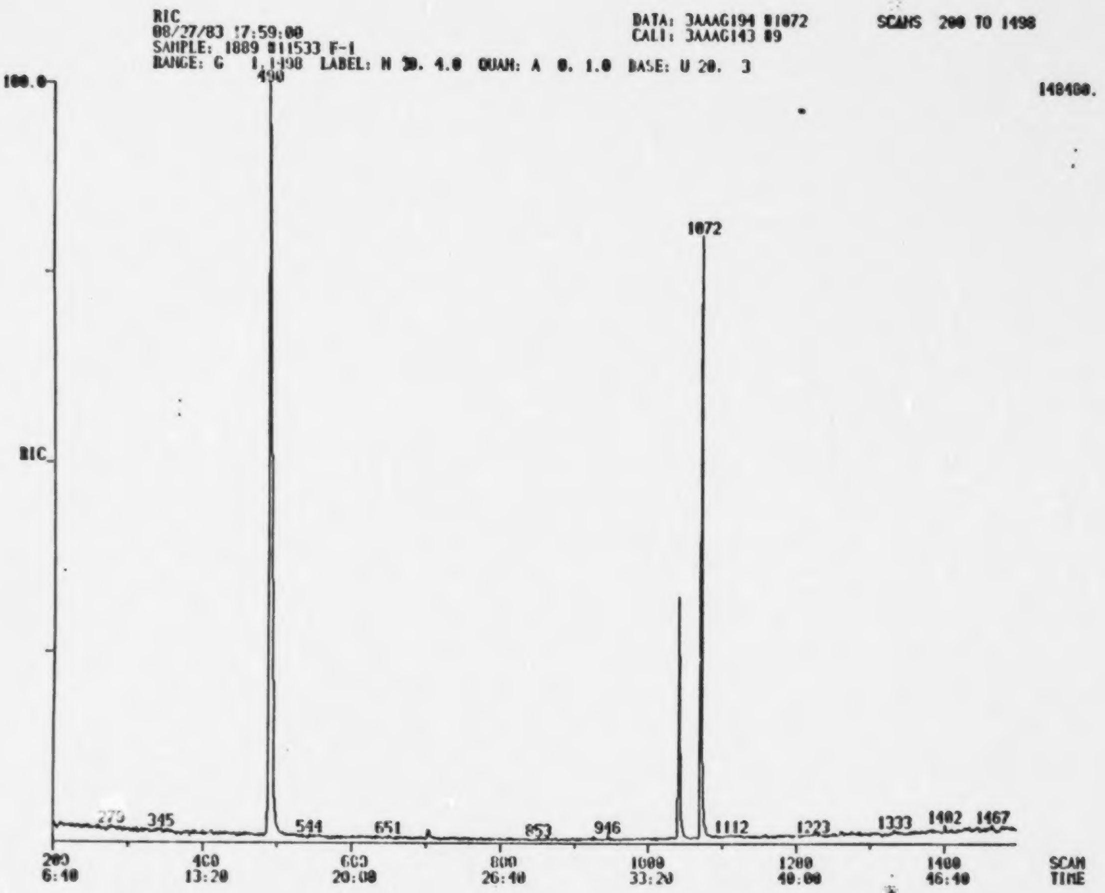


Figure 5.75. Extract 11533 (base/neutral), fraction 1.

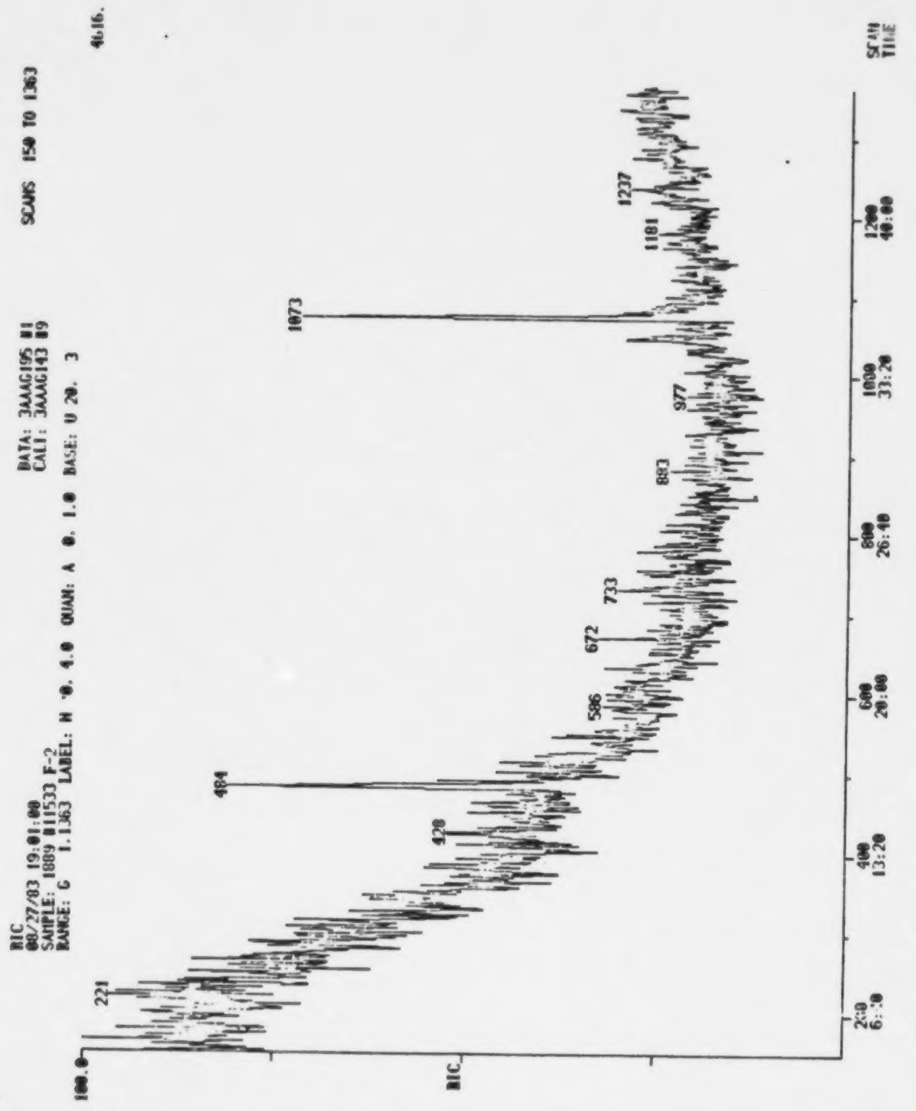


Figure 5.76. Extract 11533 (base/neutral), fraction 2.

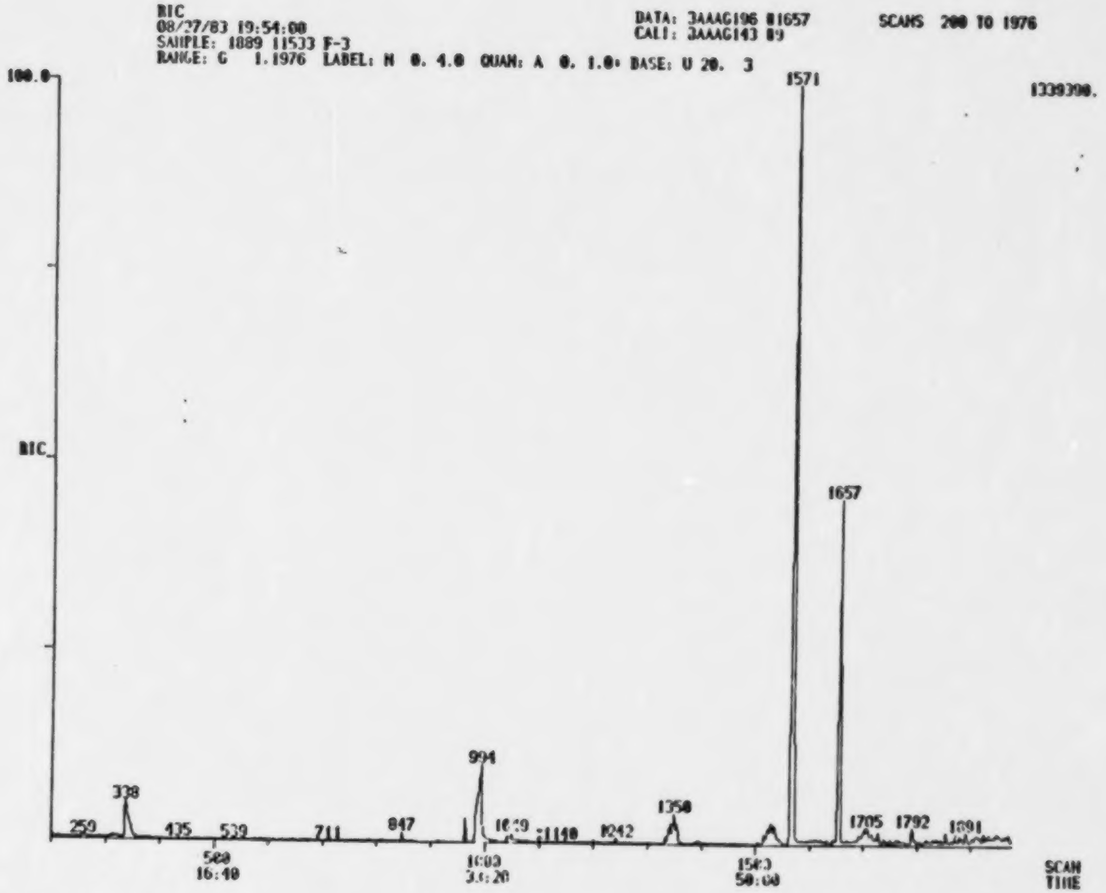


Figure 5.77. Extract 11533 (base/neutral), fraction 3.

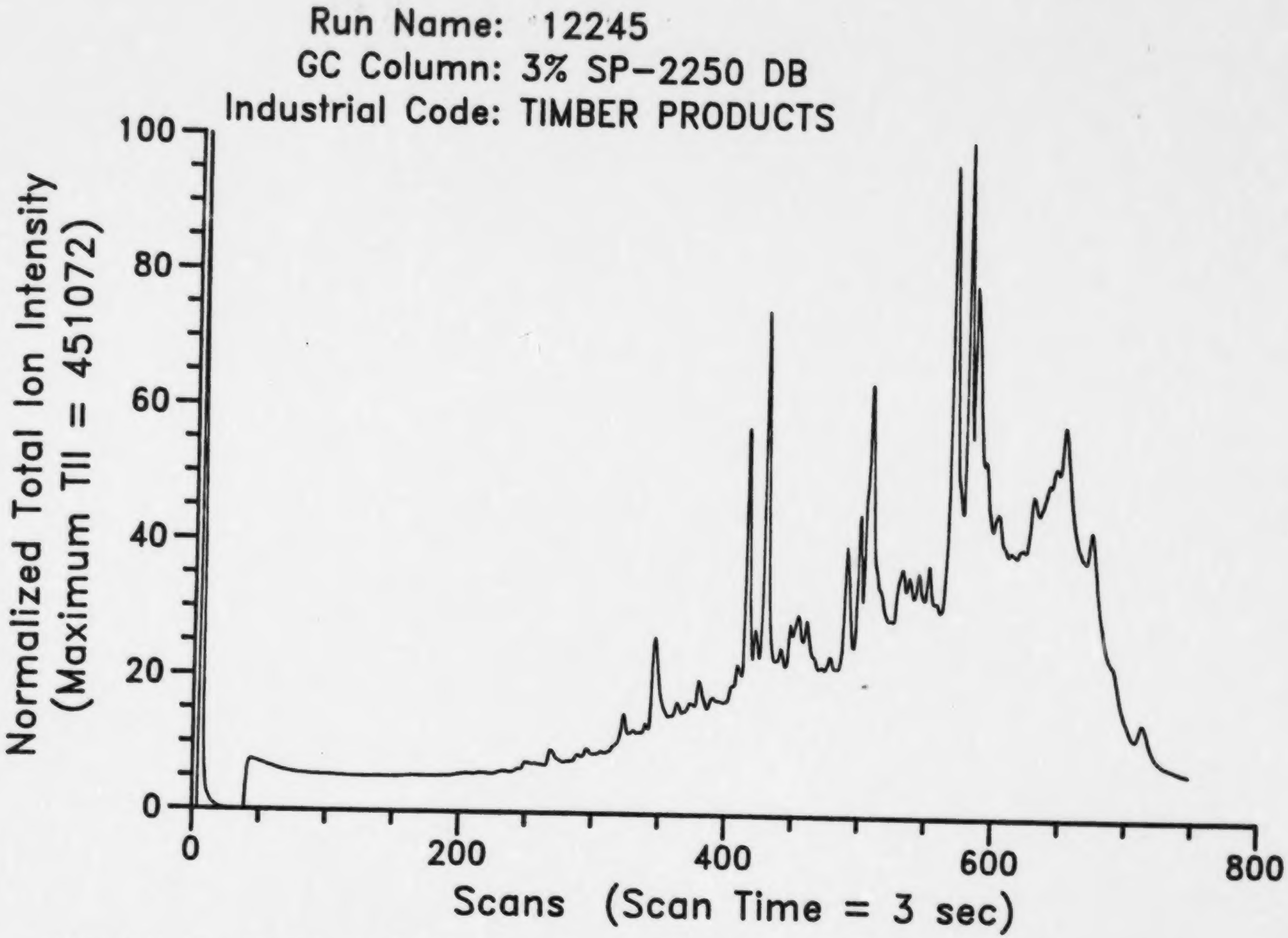


Figure 5.78. Packed column chromatogram, extract 12245 (base/neutral), timber products industry.

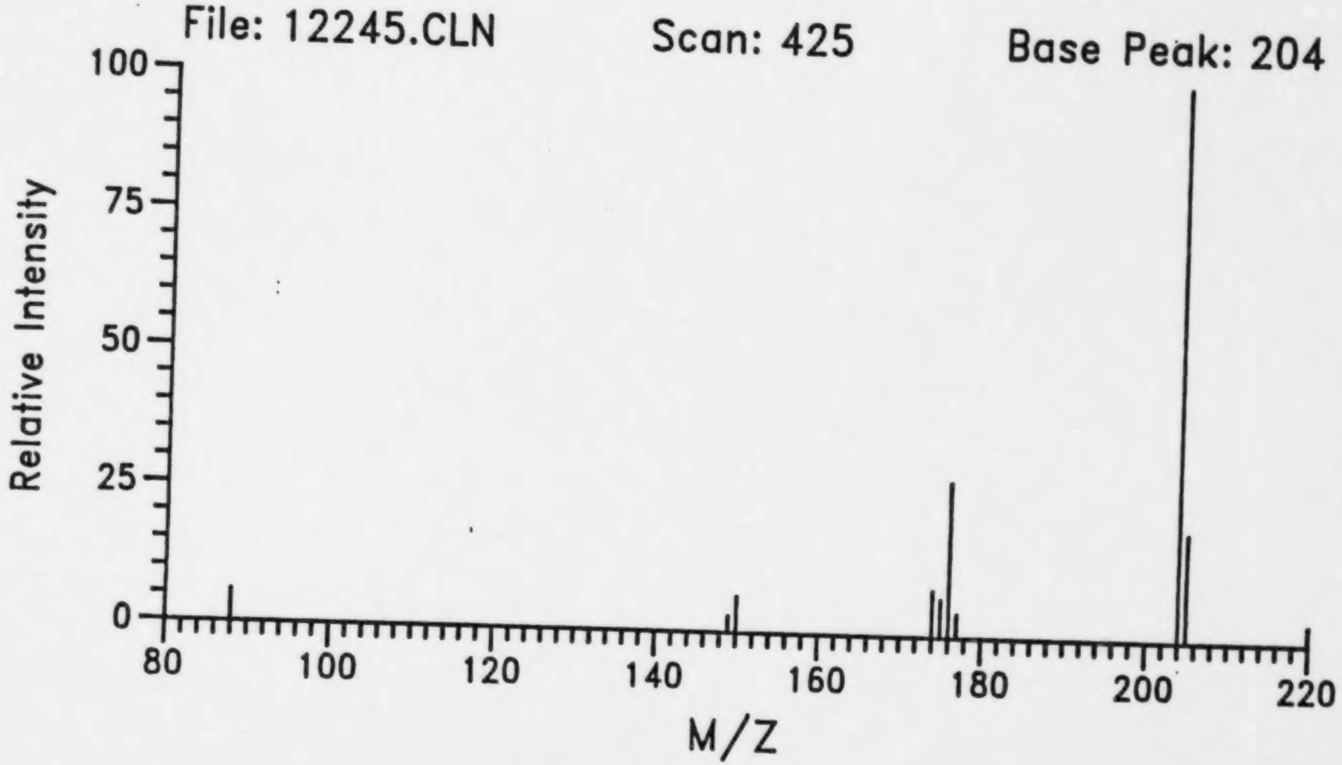


Figure 5.79. Extract 12245 (base/neutral), timber products industry. Frequency of occurrence: 15.

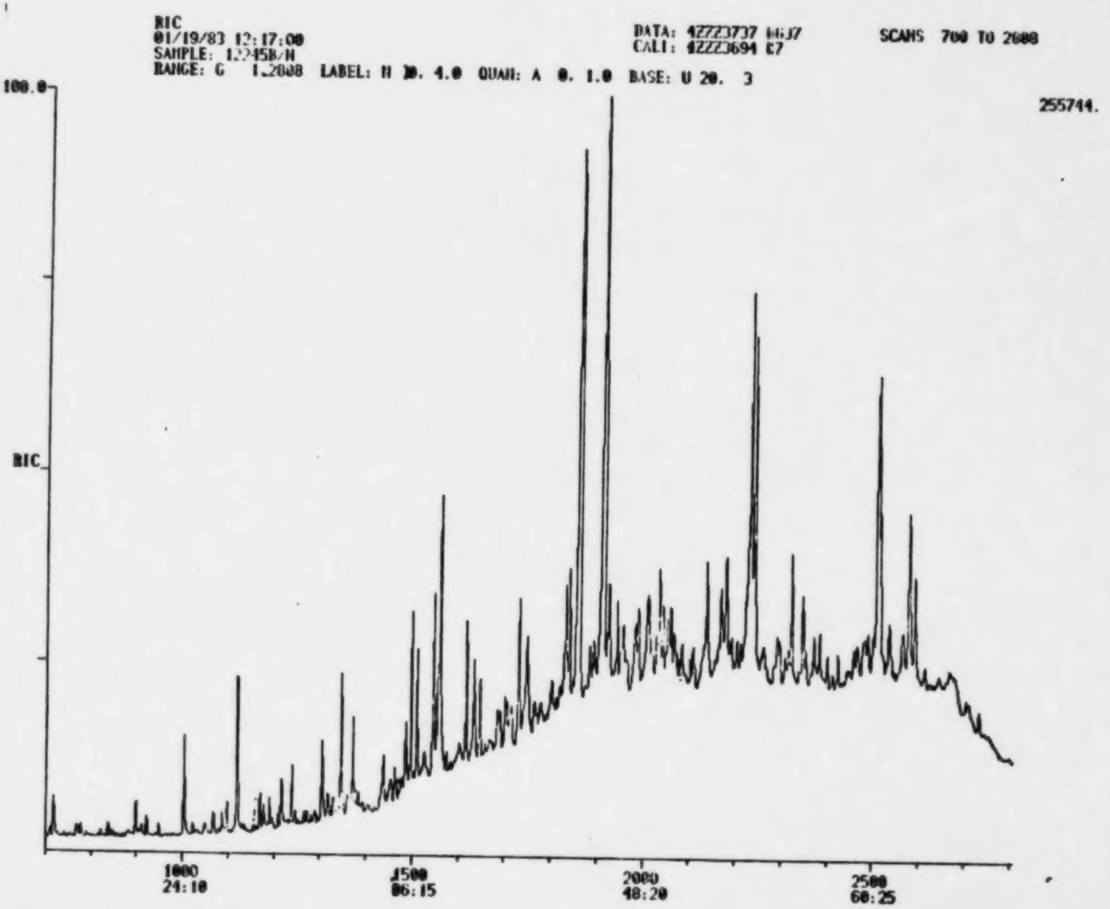


Figure 5.80. Capillary chromatogram of extract 12245 (base/neutral), timber products industry.

as obtained from the capillary chromatogram is shown in Figure 5.81. Accurate mass measurements at mass 204 and mass 176 present four possibilities: $C_{14}H_8N_2$ (error, 7.7 mmu), $C_{15}H_8O$ (error, -3.5 mmu), $C_9H_8N_4O_2$ (error, 3.7 mmu), and $C_8H_{12}O_6$ (error, 2.4 mmu). The logical transitions for production of the $(M-28)^{+\cdot}$ peak are loss of N_2, CO, or C_2H_4. The loss of a molecule of nitrogen is mass spectrometrically possible but unusual and has been observed only in systems where the two nitrogen atoms are originally bonded together. Loss of CO is far more common, and this loss of CO is indicated by accurate mass measurement for the latter three possibilities. The compound containing only C, H, and N also has the highest value for error. Therefore, the compound probably contains only C, H, and O, or possibly C, H, N, and O; the compound in any case contains oxygen. The extract was fractionated in the hope of finding the compound of interest as a major constituent in its fraction in order to permit analysis by GC/FT-IR. Capillary chromatograms of two fractions are shown in Figures 5.82 and 5.83. Since the compound of interest was observed as a very minor constituent of fraction 2, the possibility of GC/FT-IR analysis was precluded. The third fraction was not analyzed. A short description of the compounds observed in the two fractions is presented in Table 5.8. Since the compound of interest is apparently observed at several elution times in fraction 2, there must be the possibility of isomerism (see Figure 5.84).

Extract 12316 (Base/Neutral), Timber Products Industry, Wet Sludge

The packed column chromatogram of extract 12316 (base/neutral) is shown in Figure 5.85. The mass spectra of the compounds of interest are presented in Figures 5.86 and 5.87. The mass spectra of the compounds of interest as obtained from the capillary analysis are presented in Figures 5.88 and 5.89. An ion chromatogram of masses 178 and 229 suggests (Figure 5.90) that the mass spectrum of Figure 5.87 is a composite since the profiles of mass 178 and mass 229 are not the same. When the extract was fractionated and the three fractions analyzed (Figures 5.91-5.93), the spectrum was deconvoluted, and only phenanthrene was observed. The other compound of interest was not found after the fractionation. A short description of the compounds observed in the three fractions is

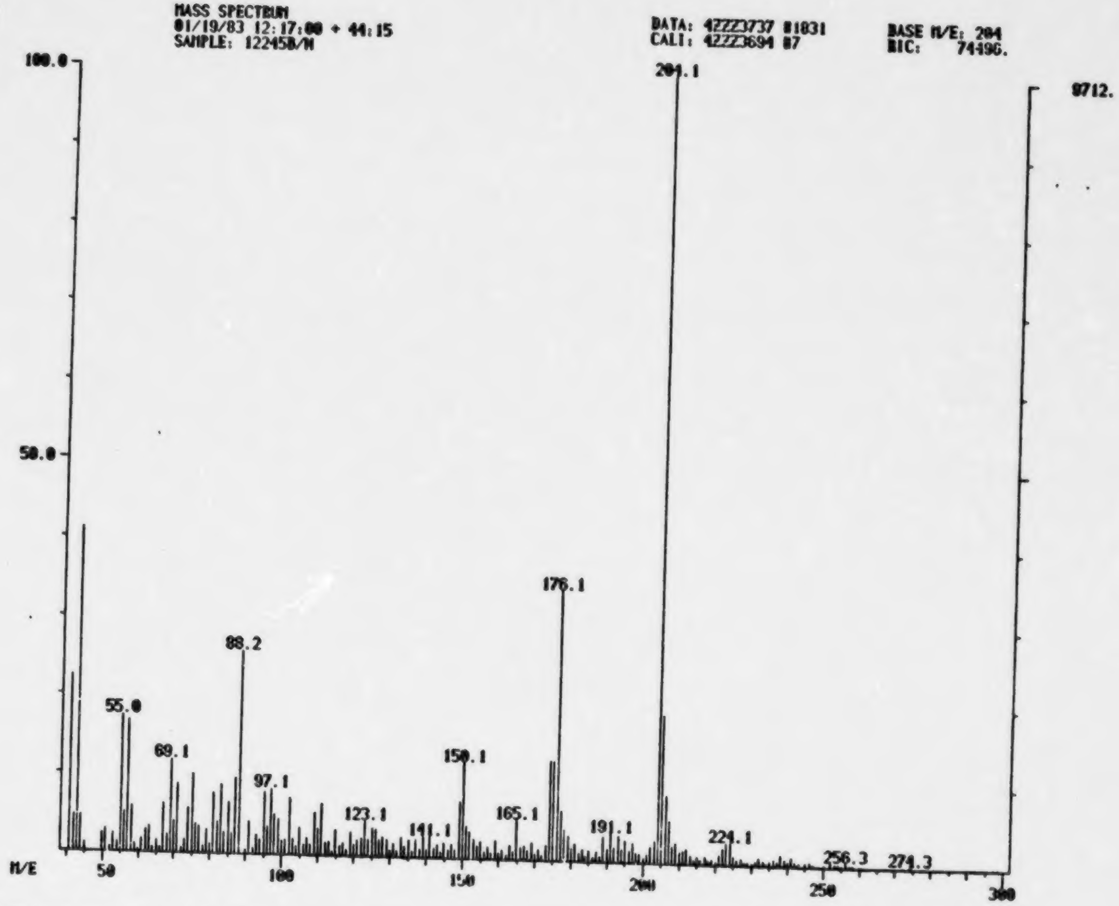


Figure 5.81. Mass spectrum of EPA compound of interest, extract 12245 (base/neutral), timber products industry, scan #1831.

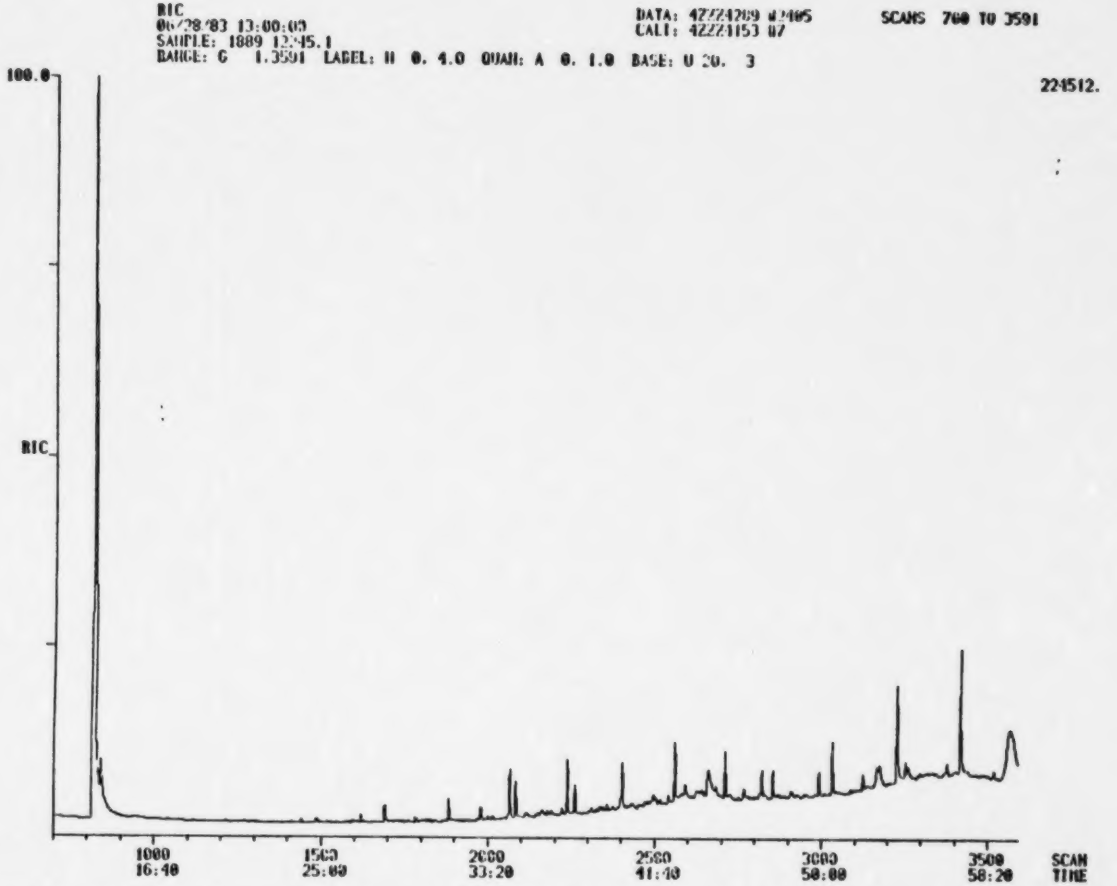


Figure 5.82. Capillary chromatogram of extract 12245 (base/neutral), fraction 1.

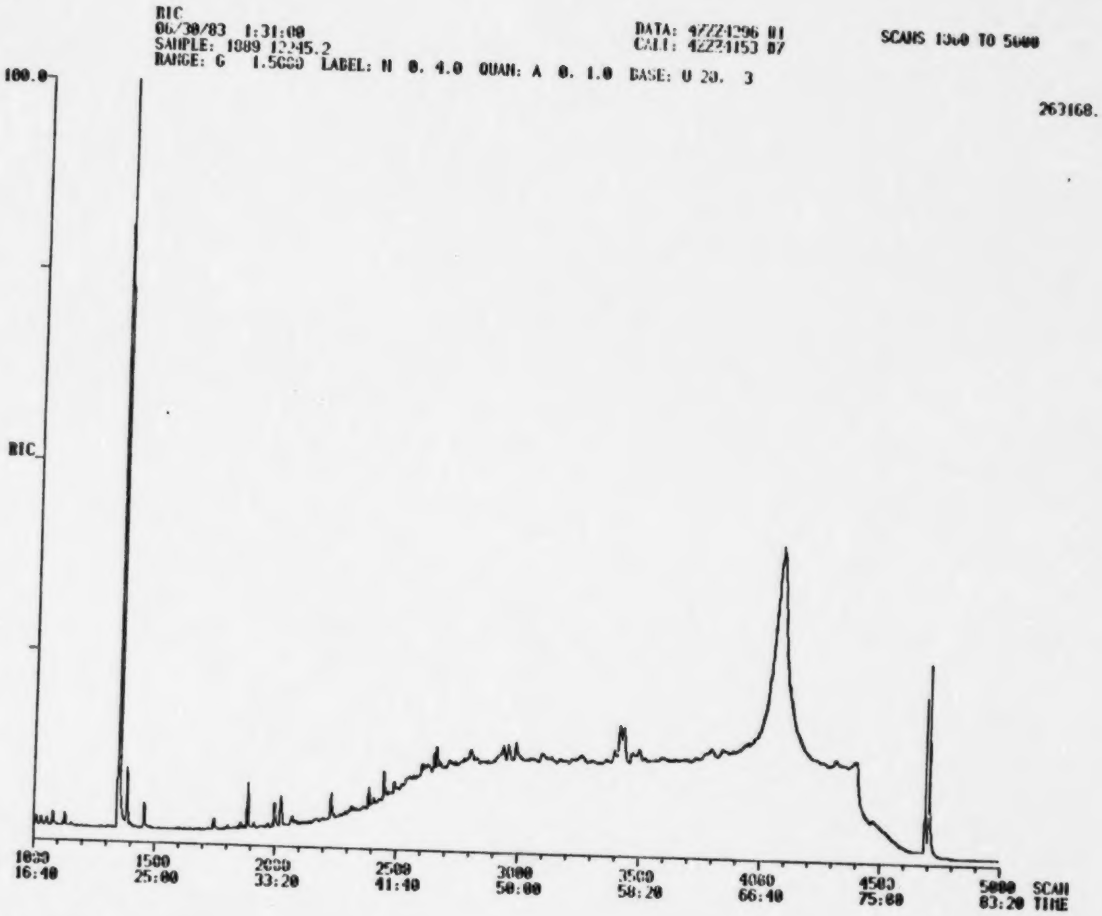


Figure 5.83. Capillary chromatogram of extract 12245 (base/neutral), fraction 2.

Table 5.8. Compounds observed in fractions of Extract 12245 (base/neutral)

	Compound	Scan	FIT
Fraction 1			
	heptadecane	2067	973
	phenanthrene	2129	983
	octadecane	2240	977
	di-isobutyl phthalate	2280	927
	9,10-anthracenedione	2423	960
	fluoranthene	2581	995
	pyrene	2661	949
Fraction 2			
	2-fluorotoluene	1353	800
	hexyl pentyl ether	1889	856
	ethyl 2-hydroxy-9-octadecenoate	4077	948

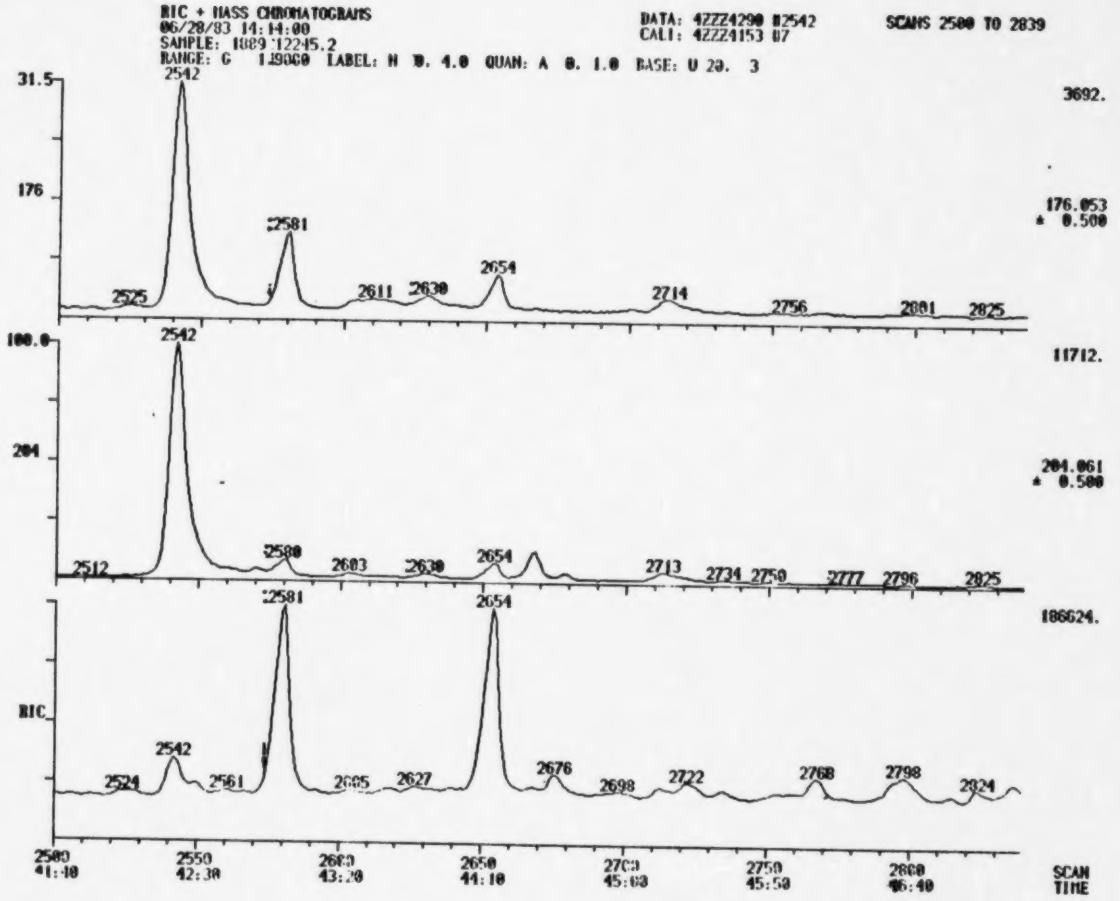


Figure 5.84. Extracted ion current profile, m/z 176 and 204, extract 12245 (base/neutral), fraction 2.

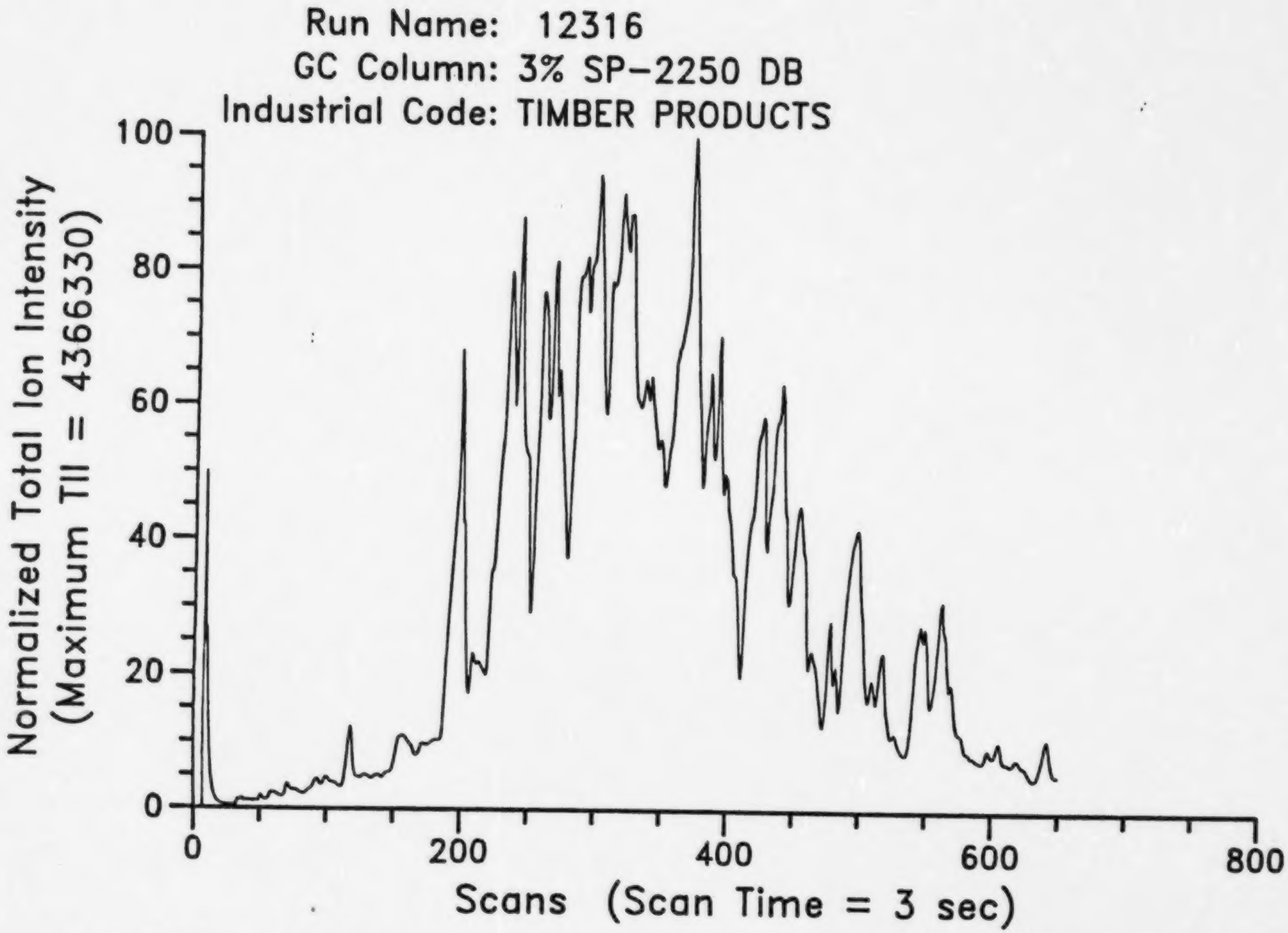


Figure 5.85. Packed column chromatogram, extract 12316 (base/neutral), timber products industry.

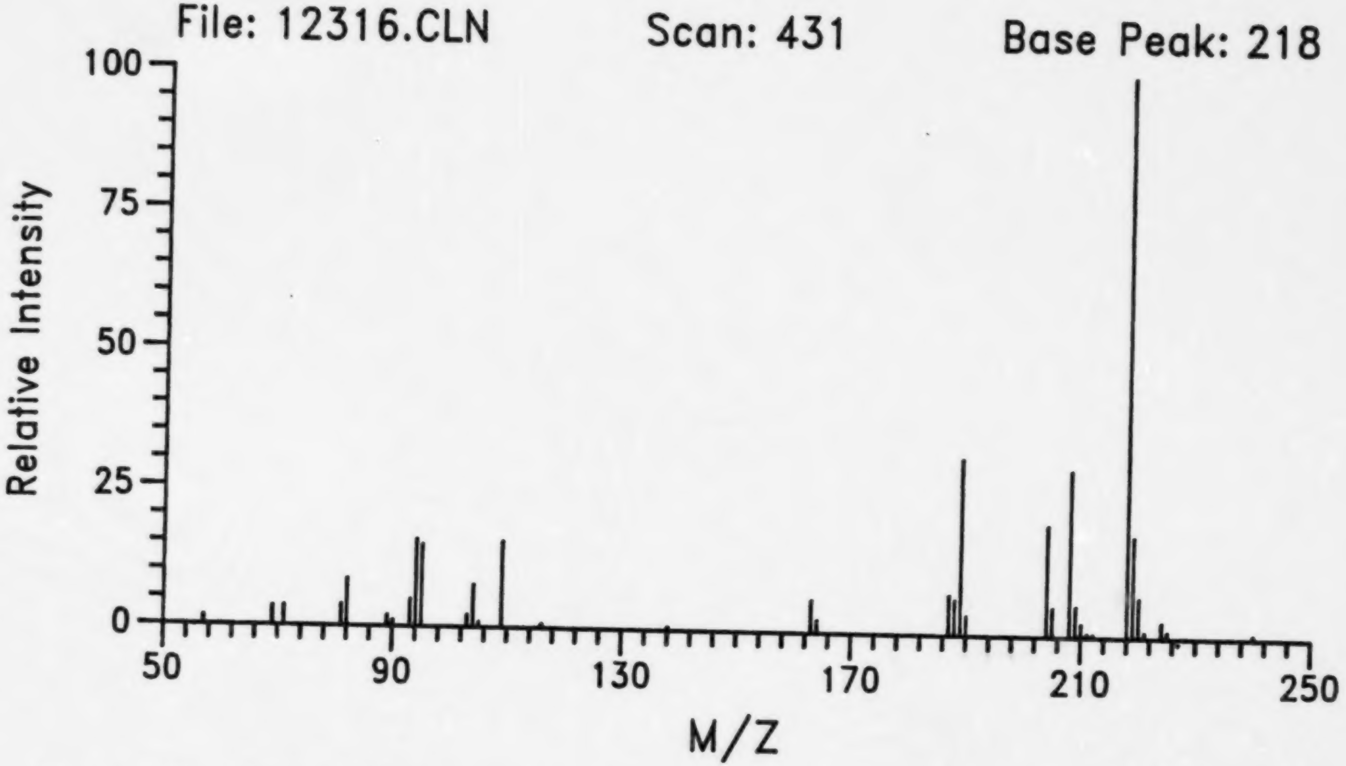


Figure 5.86. Extract 12316 (base/neutral), timber products industry. Frequency of occurrence: 11.

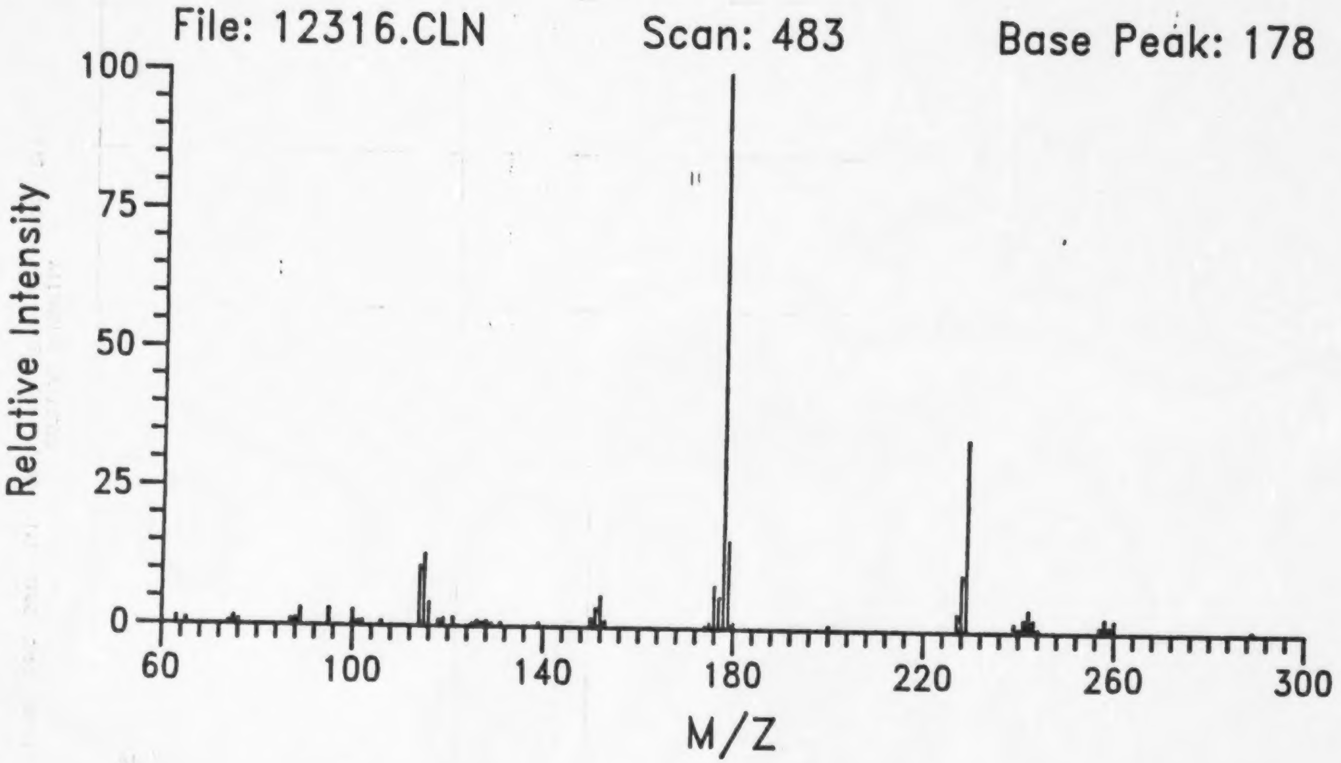


Figure 5.87. Extract 12316 (base/neutral), timber products industry. Frequency of occurrence: 11.

```
RUN IDENTIFICATION 1009 R12316 EPA*3506 B/N
SPECTRA FILE NAME AAD611
FILE POSITION    519
BACKGROUND    516
MAXIMUM INTENSITY   2634         x OF TOTAL ION    33.6
OUTPUT MASS RANGE    40 TO     492
SCAN SPEED       2
MASS          218    189    219    244    232    215    187    209    109    222
INTENSITY   10000   1533   1442   1359    994    880    774    720    607    607
```

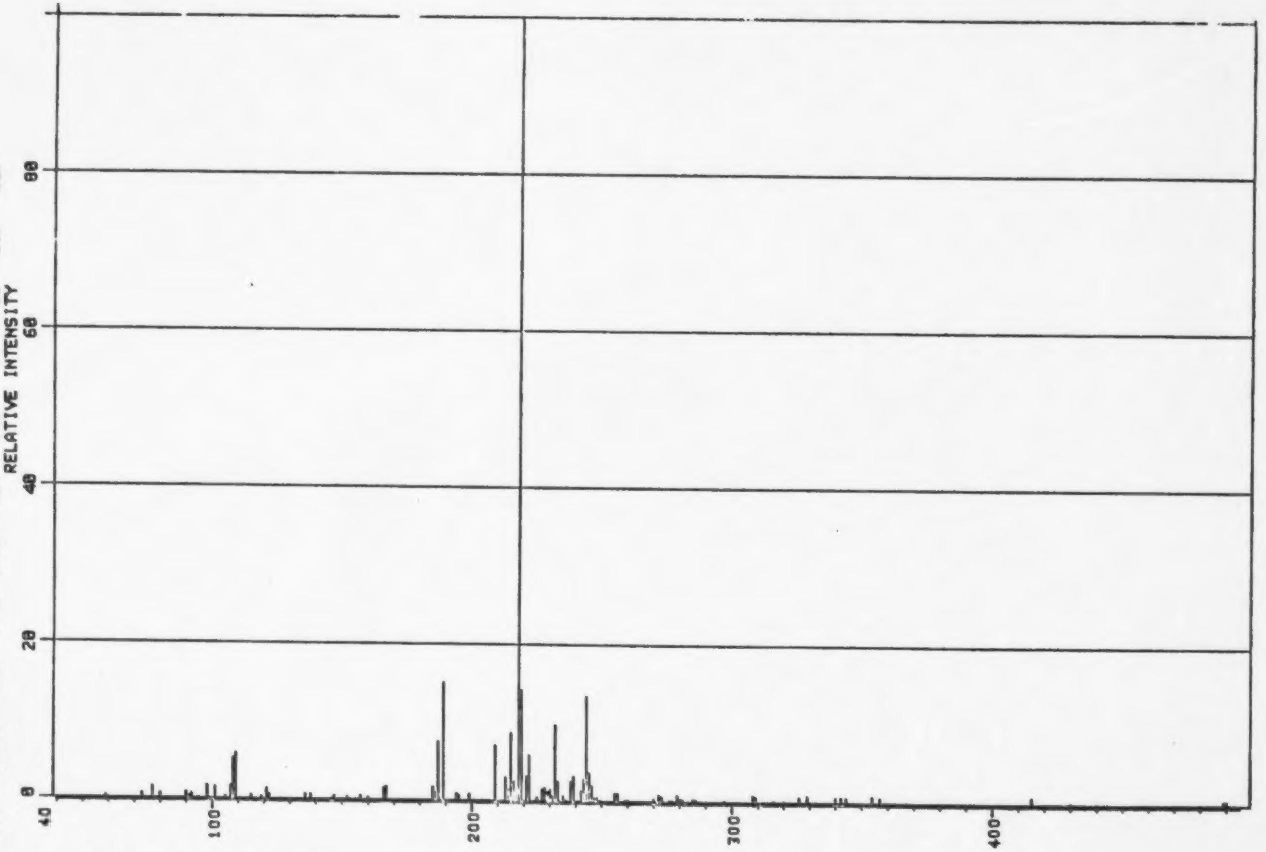


Figure 5.88. Mass spectrum of EPA compound of interest, extract 12316 (base/neutral), timber products industry, scan #579.

```
RUN IDENTIFICATION 1889 R12316 EPA•3586 B/N
SPECTRA FILE NAME AAD611
FILE POSITION    612
BACKGROUND    628
MAXIMUM INTENSITY    9242        x OF TOTAL ION    24.6
OUTPUT MASS RANGE      48 TO    492
SCAN SPEED      2
MASS            178   229   217   179   228   176   115   177   244   116
INTENSITY     10000  3445  2036  1718  1311   939   690   597   584   573
```

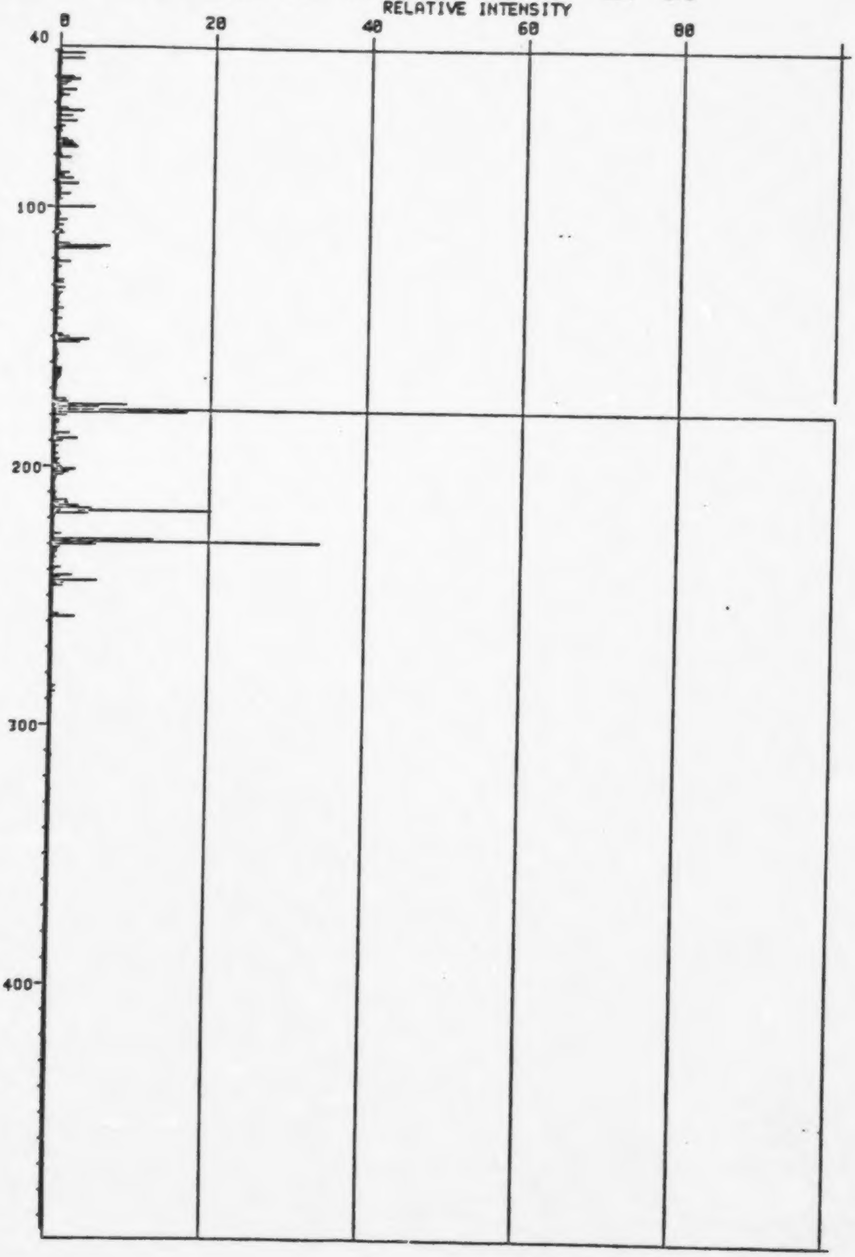


Figure 5.89. Mass spectrum of EPA compound of interest, extract 12316 (base/neutral), timber products industry, scan #612.

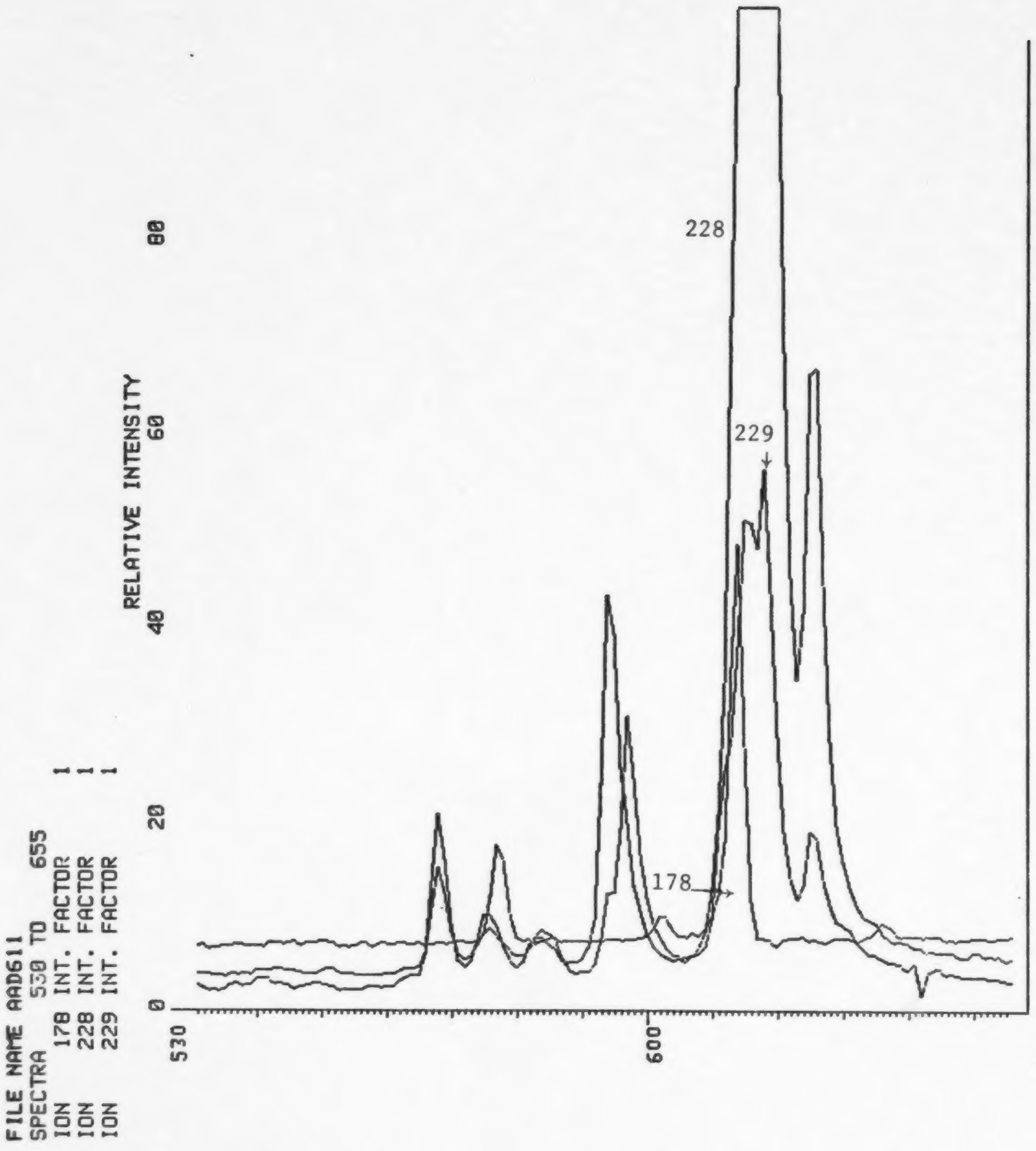


Figure 5.90. Extracted ion current profile m/z 178, 228, 229.

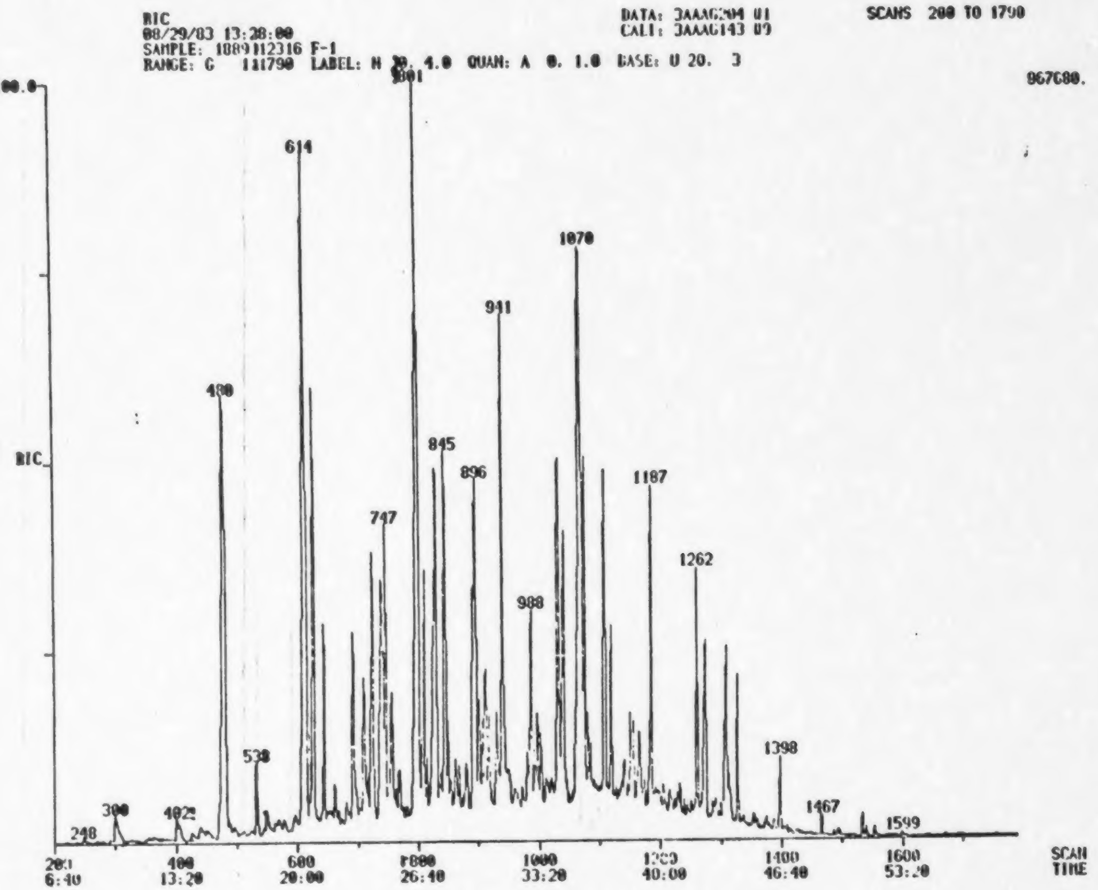


Figure 5.91. Capillary chromatogram of extract 12316 (base/neutral), fraction 1.

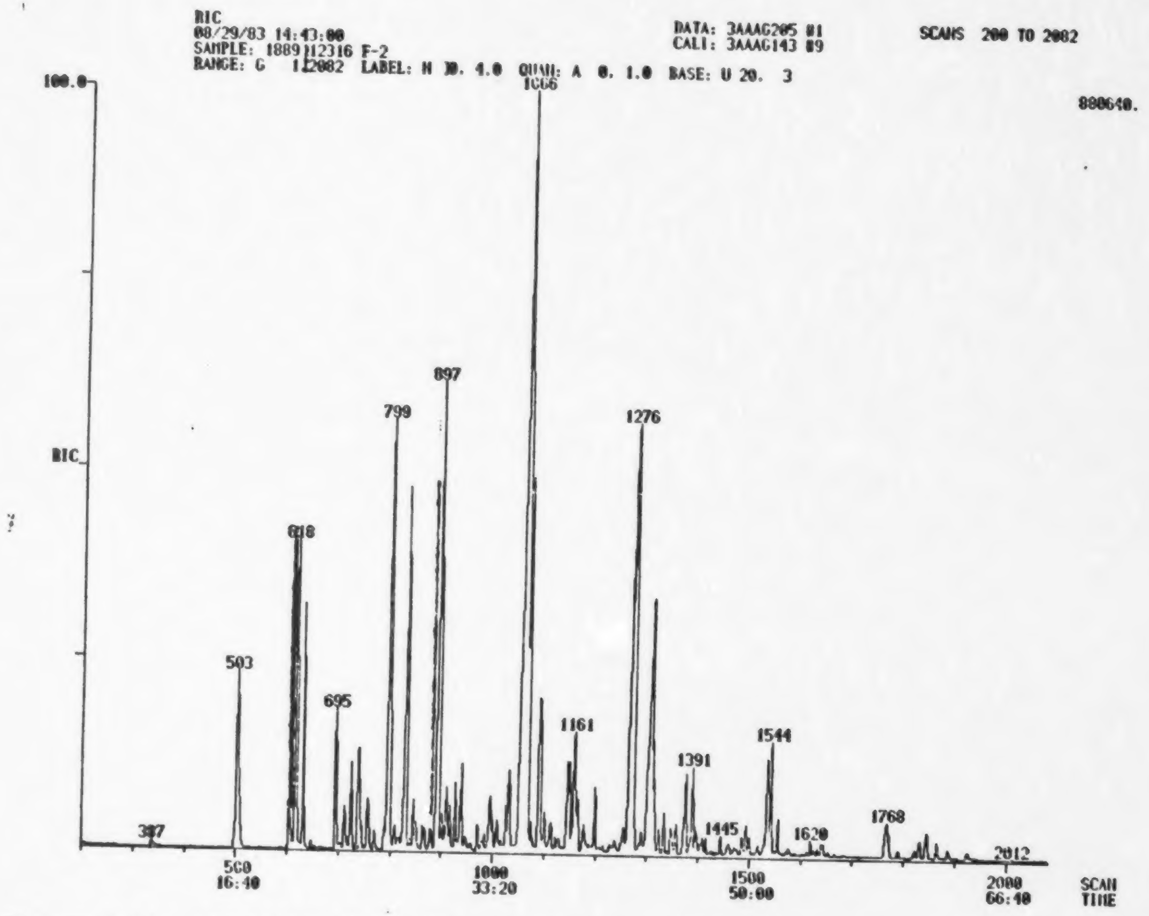


Figure 5.92. Capillary chromatogram of extract 12316 (base/neutral), fraction 2.

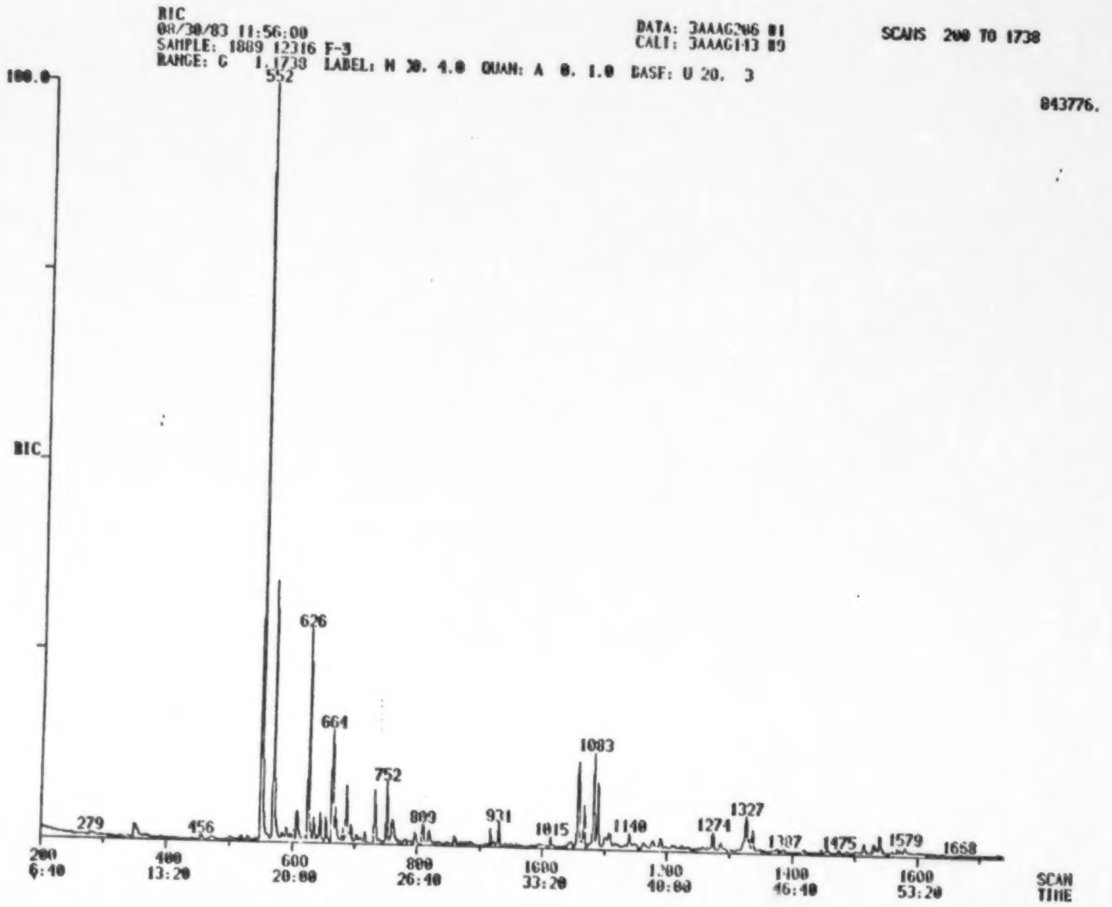


Figure 5.93. Capillary chromatogram of extract 12316 (base/neutral), fraction 3.

presented in Table 5.9. Again note that although there is substantial crosstalk between the first two fractions, the polar fraction seems to be cleanly separated from the less polar materials.

Extract 13230 (Acid), Mechanical Products Industry, Untreated Effluent

The packed column chromatogram of extract 13230 (acid) is shown in Figure 5.94. The mass spectrum of the compound of interest is presented in Figure 5.95. The capillary chromatogram of extract 13230 (acid) is shown in Figure 5.96. The mass spectrum of the compound of interest as observed from the capillary chromatogram is shown in Figure 5.97. Accurate mass measurement with consideration of C, H, N, O, Cl, S, and P in the mass table produces a list of more than 50 possibilities. The presence of phosphorus is inferred from an ion of mass 47 in the mass spectrum. The ion profile at $\underline{m}/\underline{z}$ 179/181 and 235/237 suggests the presence of chlorine. The ions at mass 143/145 suggest the presence of sulfur. Accurate mass measurement possibilities can thus be limited to $C_8H_9O_2ClSP$ (error, 0.9 mmu) for $\underline{m}/\underline{z}$ 235, and C_4HO_2ClSP (error, -8.8 mmu) for $\underline{m}/\underline{z}$ 179. Methane chemical ionization produces an ion at mass 291, which could be either an $(M+1)^+$ or $(M-1)^+$ species. If the molecular weight is 292, the most probable composition would be $C_9H_{19}Cl_2PO_2S$. The molecule is polyfunctional and relatively polar. FTIR would provide extremely useful information if the component can at least be somewhat purified and concentrated in a fraction. The extract was therefore fractionated (see Figures 5.98 and 5.99), and the compounds of interest were found in fraction 2. The major constituents of fraction 1 were hydrocarbons, of fraction 2, fatty acids. There are at least two compounds (Figure 5.100 and 5.101) similar to the compound of interest, but these are minor constituents in the fraction, so FT-IR information cannot be obtained. No definitive structure assignment can be made.

Extract 13240 (Base/Neutral), Mechanical Products Industry, Coalescent Effluent

The packed column chromatogram of extract 13240 (base/neutral) is shown in Figure 5.102. The mass spectrum of the compound of interest is presented in Figure 5.103. The capillary chromatogram of extract 13240 is shown in Figure 5.104, and two mass spectra corresponding to the EPA

Table 5.9. Compounds observed in fractions of extract 12316 (base/neutral).

Compound	Scan	Fit
Fraction 1		
naphthalene	480	989
2-methylnaphthalene	614	973
1,2-dichloroacenaphthylene	801	981
octadecane	941	951
phenanthrene	1070	986
Fraction 2		
naphthalene	618	966
1,2-dihydroacenaphthylene	799	982
dibenzofuran	833	987
1H-phenalene	897	930
anthracene	1066	982
fluoranthene	1276	969
chrysene	1544	975
Fraction 3		
isoquinoline	552	990
isoquinoline	570	996
2-methylquinoline	626	981
6-methylquinoline	664	981
benzo[h]quinoline	1059	980
benzo[h]quinoline	1083	983
9-anthracenecarbonitrile	1327	929

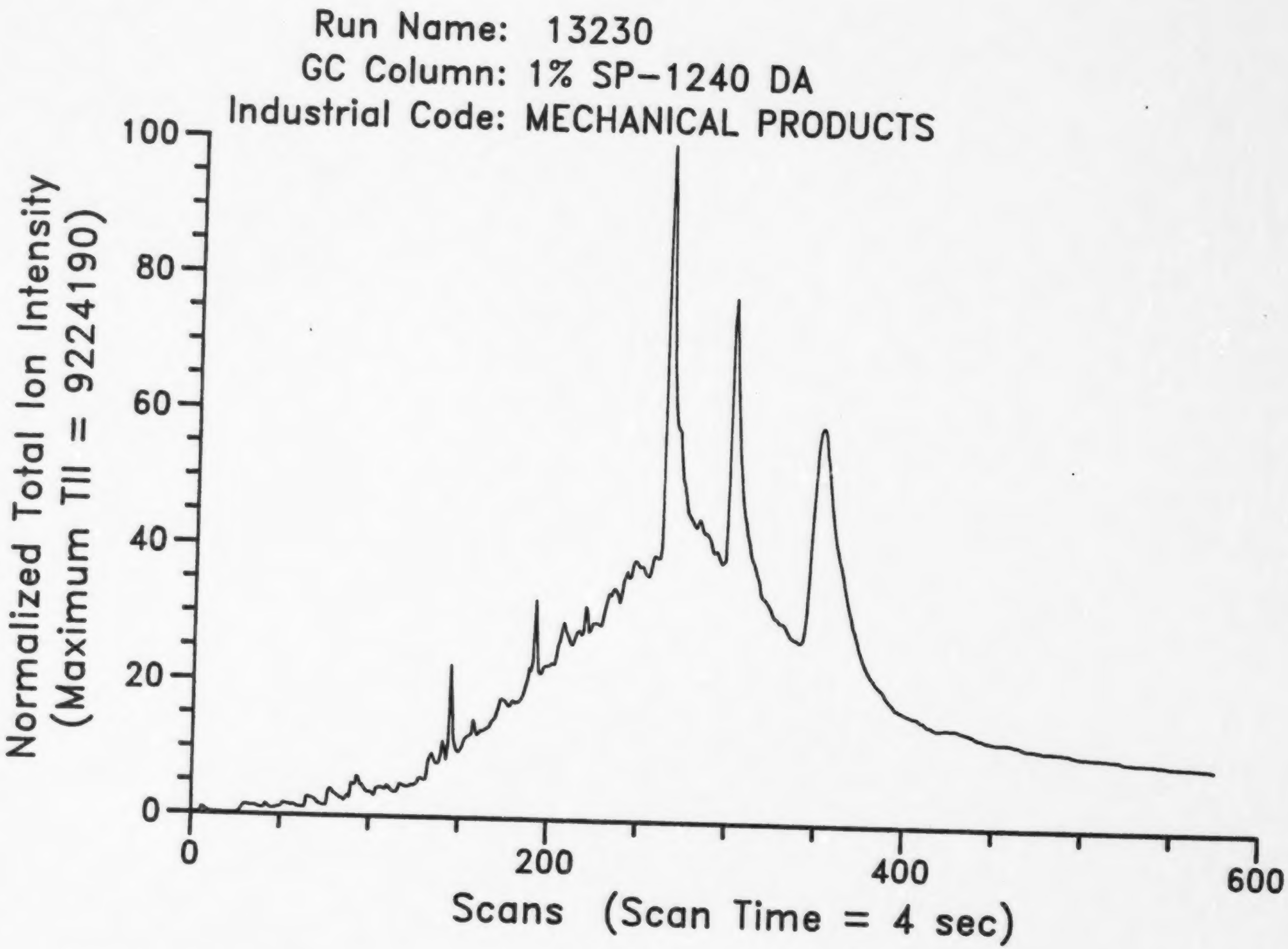


Figure 5.94. Packed column chromatogram, extract 13230 (acid), mechanical products industry.

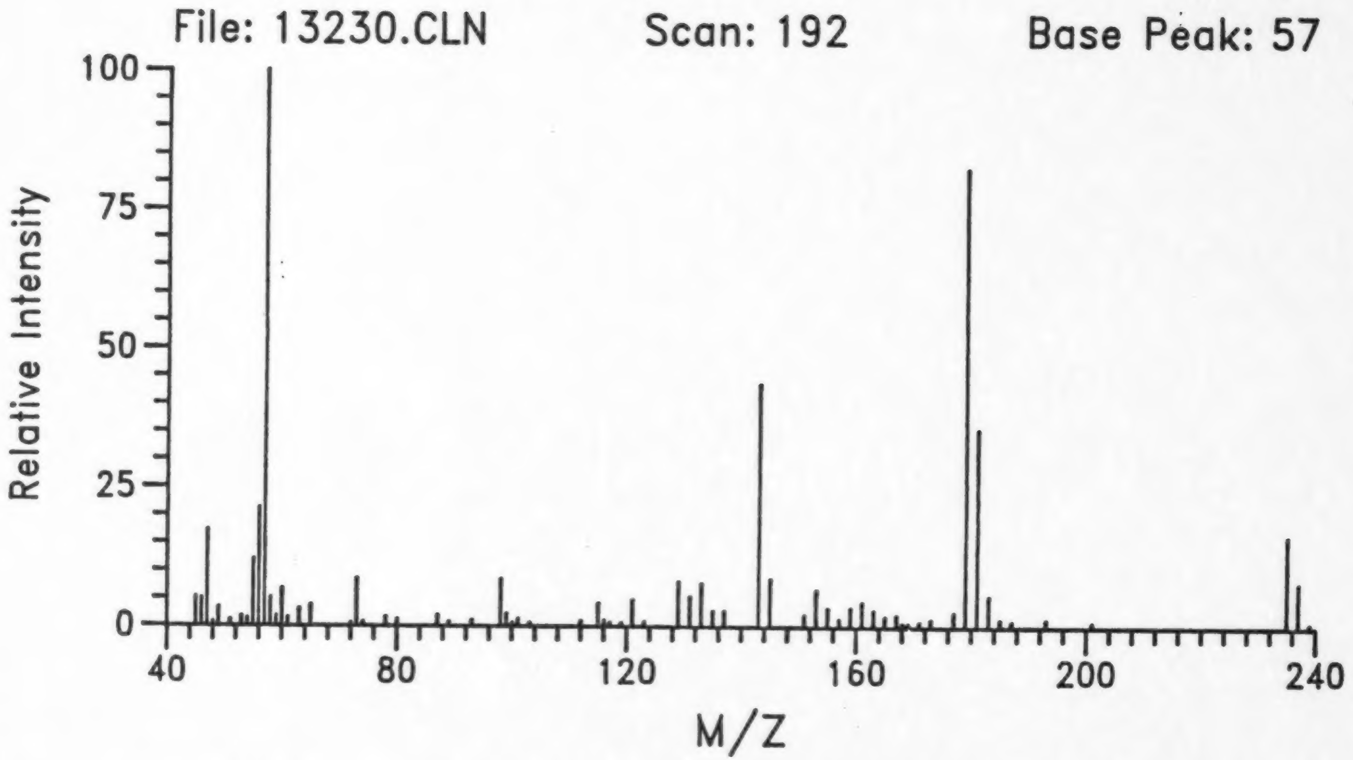


Figure 5.95. Extract 13230 (acid), mechanical products industry. Frequency of occurrence: 6.

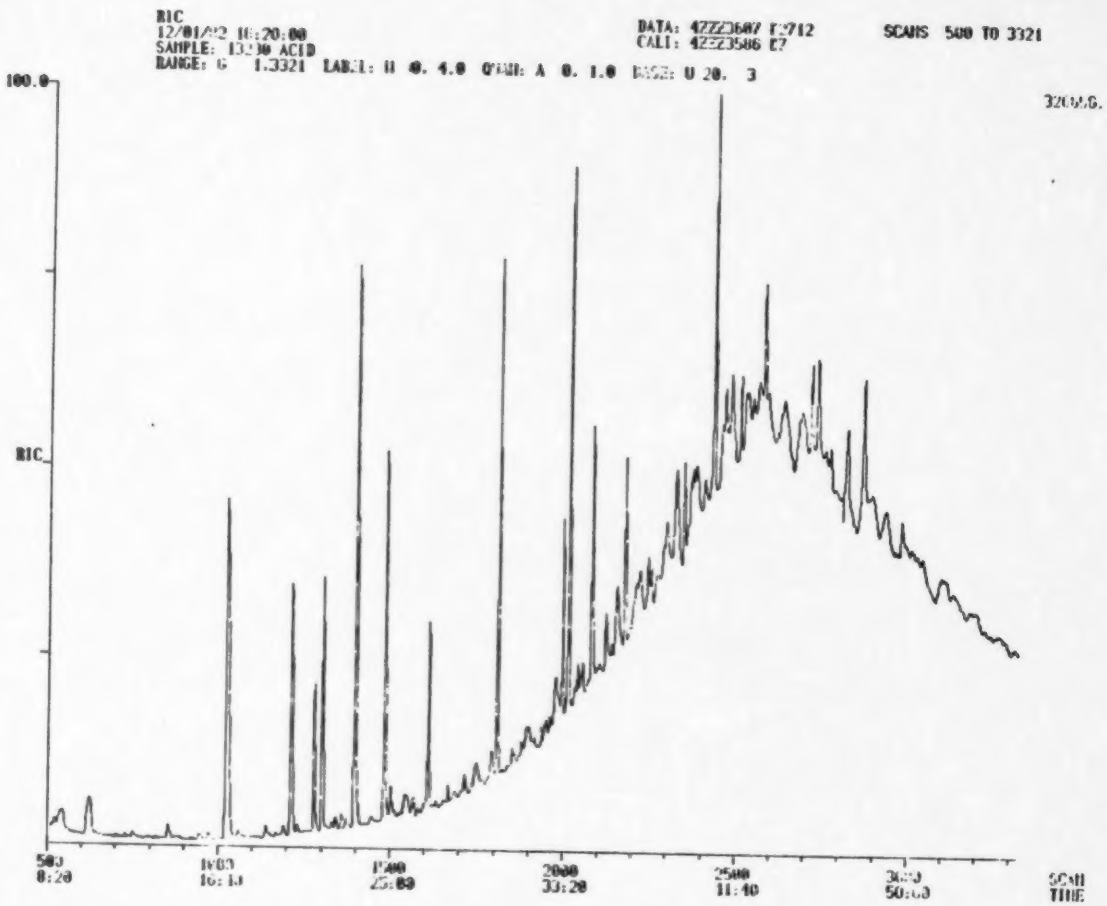


Figure 5.96. Capillary chromatogram of extract 13230 (acid), mechanical products industry.

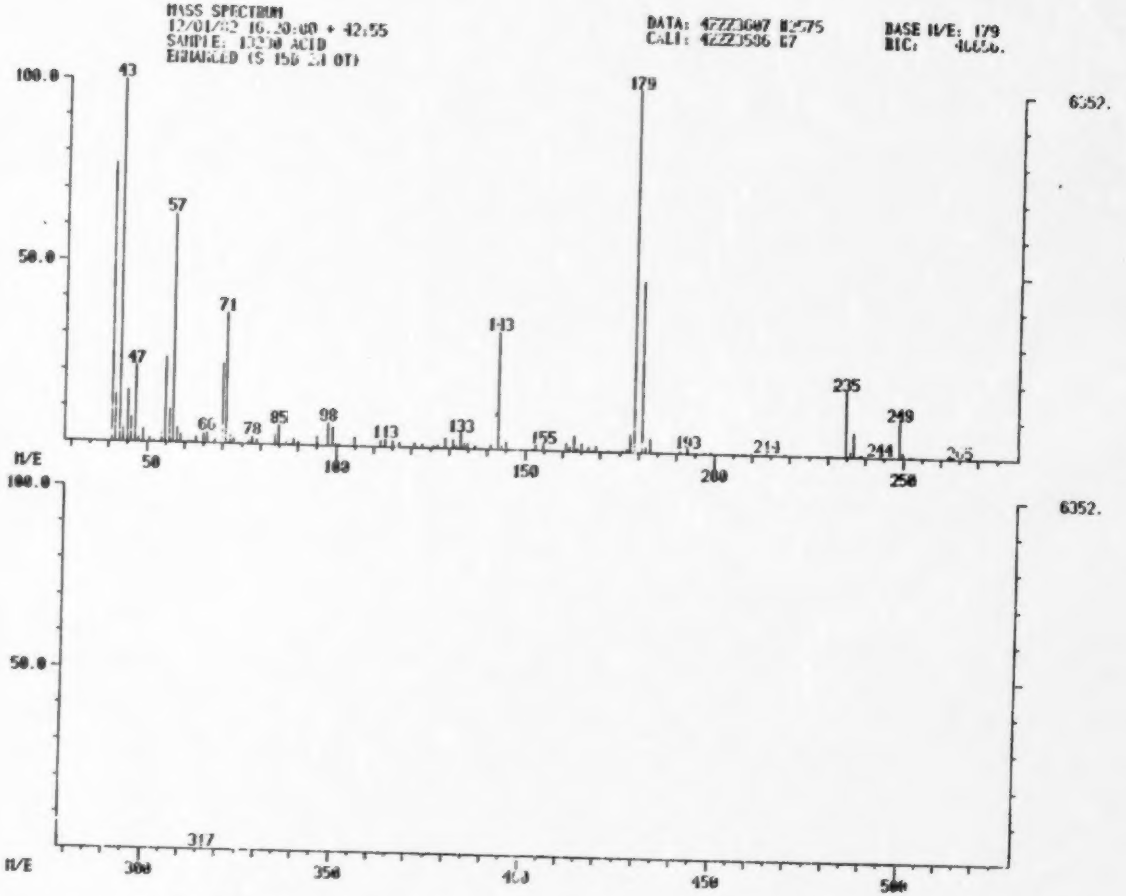


Figure 5.97. Mass spectrum of EPA compound of interest, extract 13230 (acid), mechanical products industry, scan #2575.

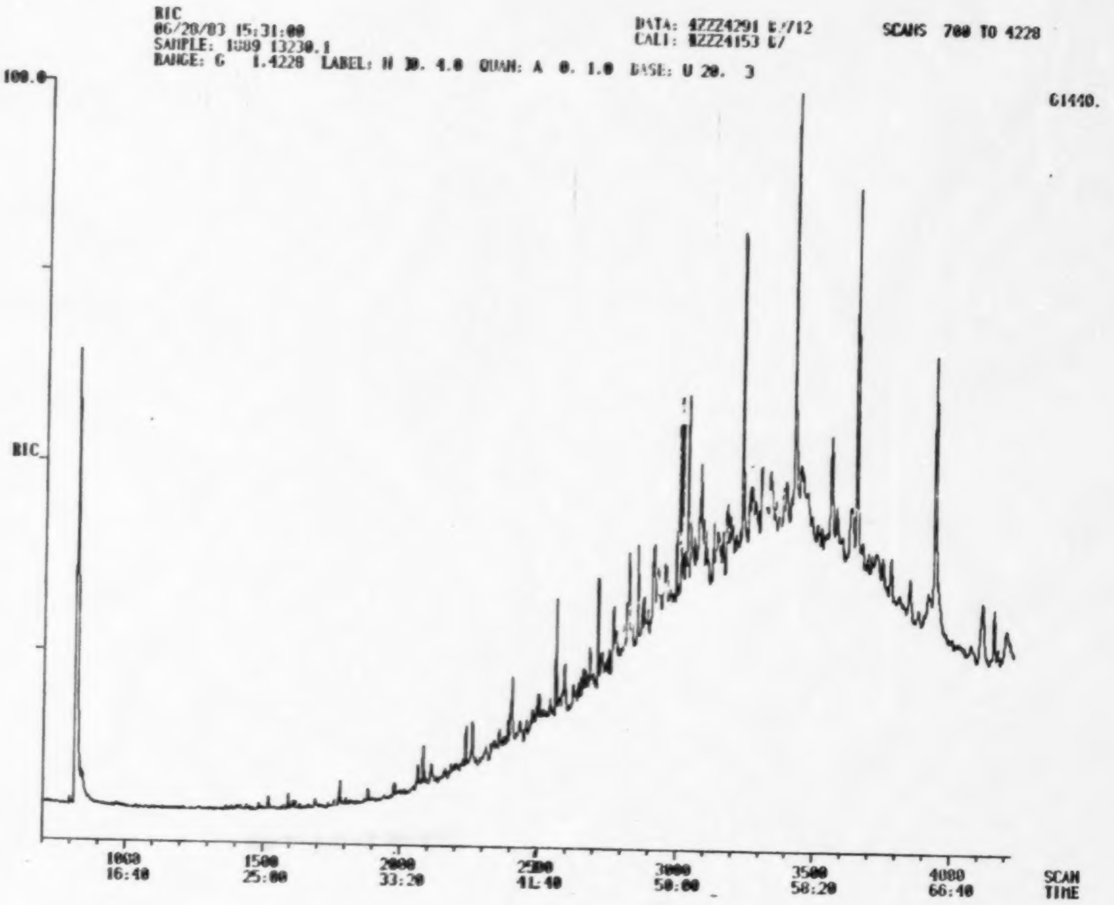


Figure 5.98. Capillary chromatogram of extract 13230 (acid), fraction 1.

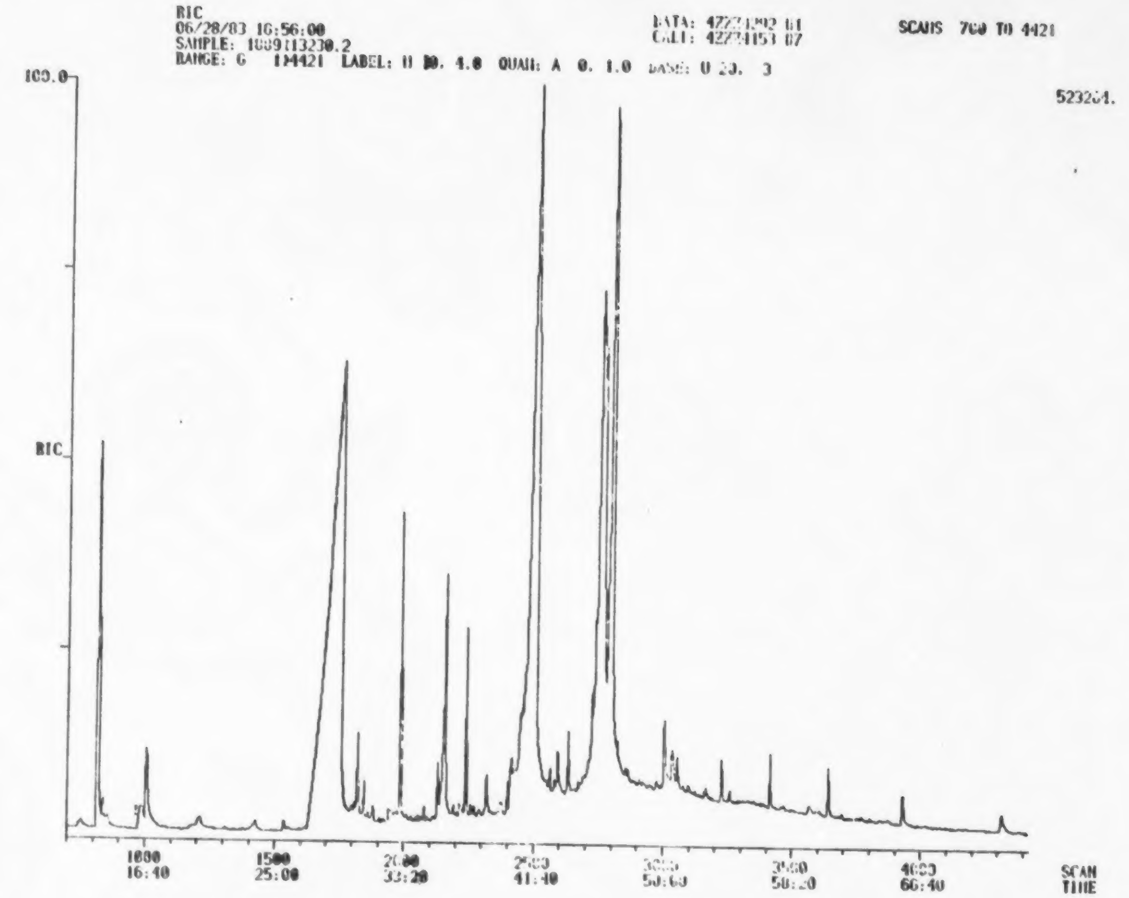


Figure 5.99. Capillary chromatogram of extract 13230 (acid), fraction 2.

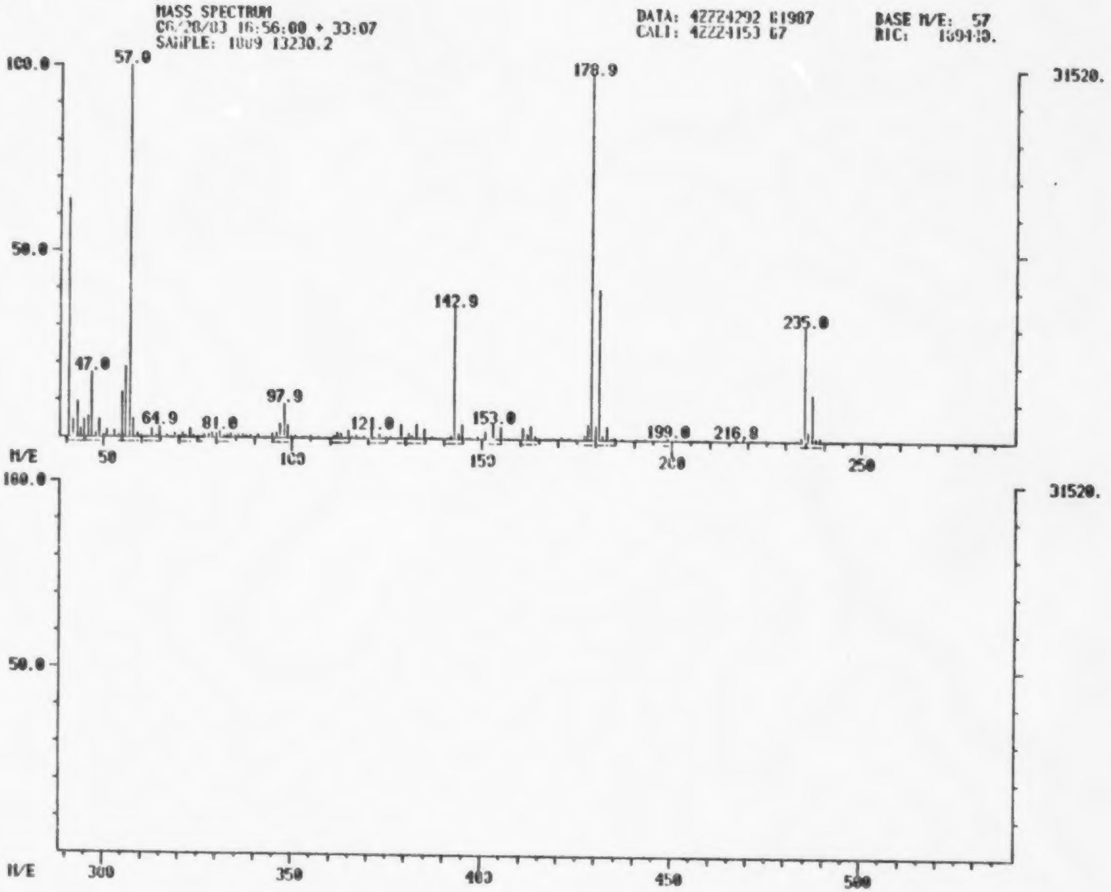


Figure 5.100. Mass spectrum of compound of interest, fraction 2, scan #1987.

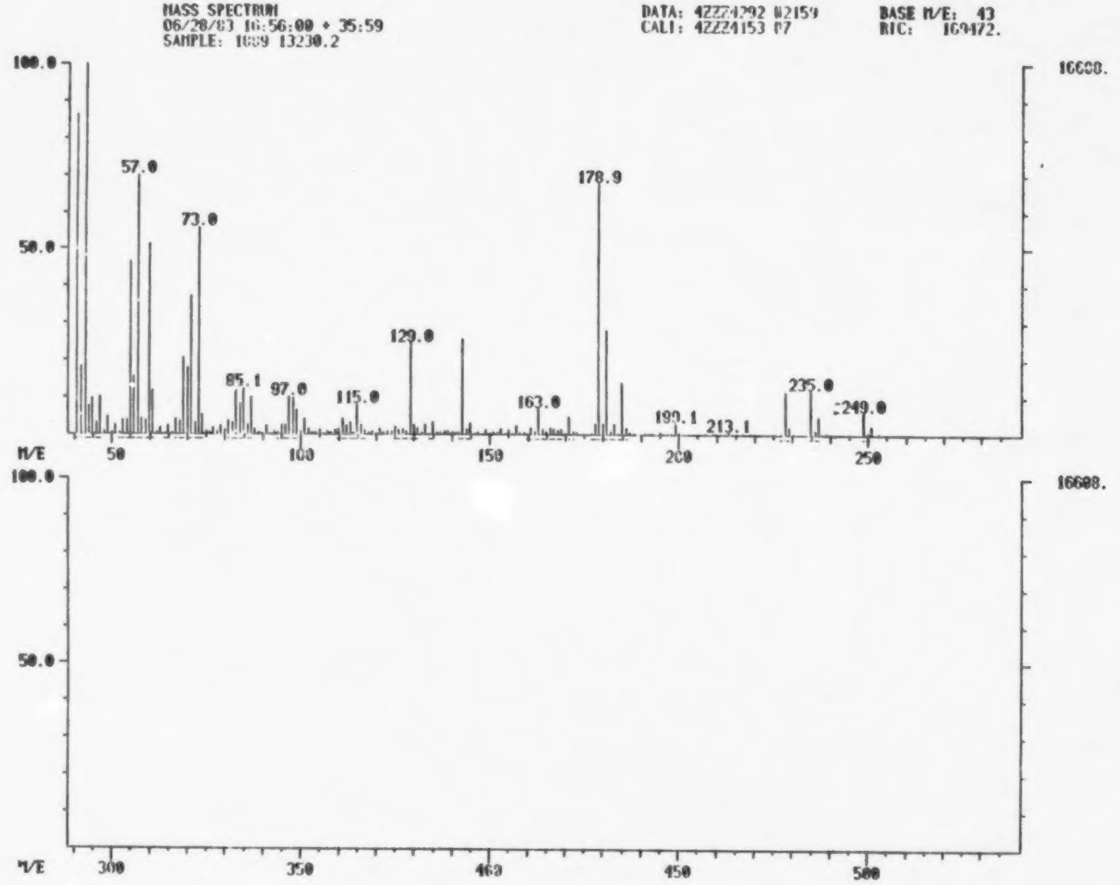


Figure 5.101. Mass spectrum of compound of interest, fraction 2., scan #2159.

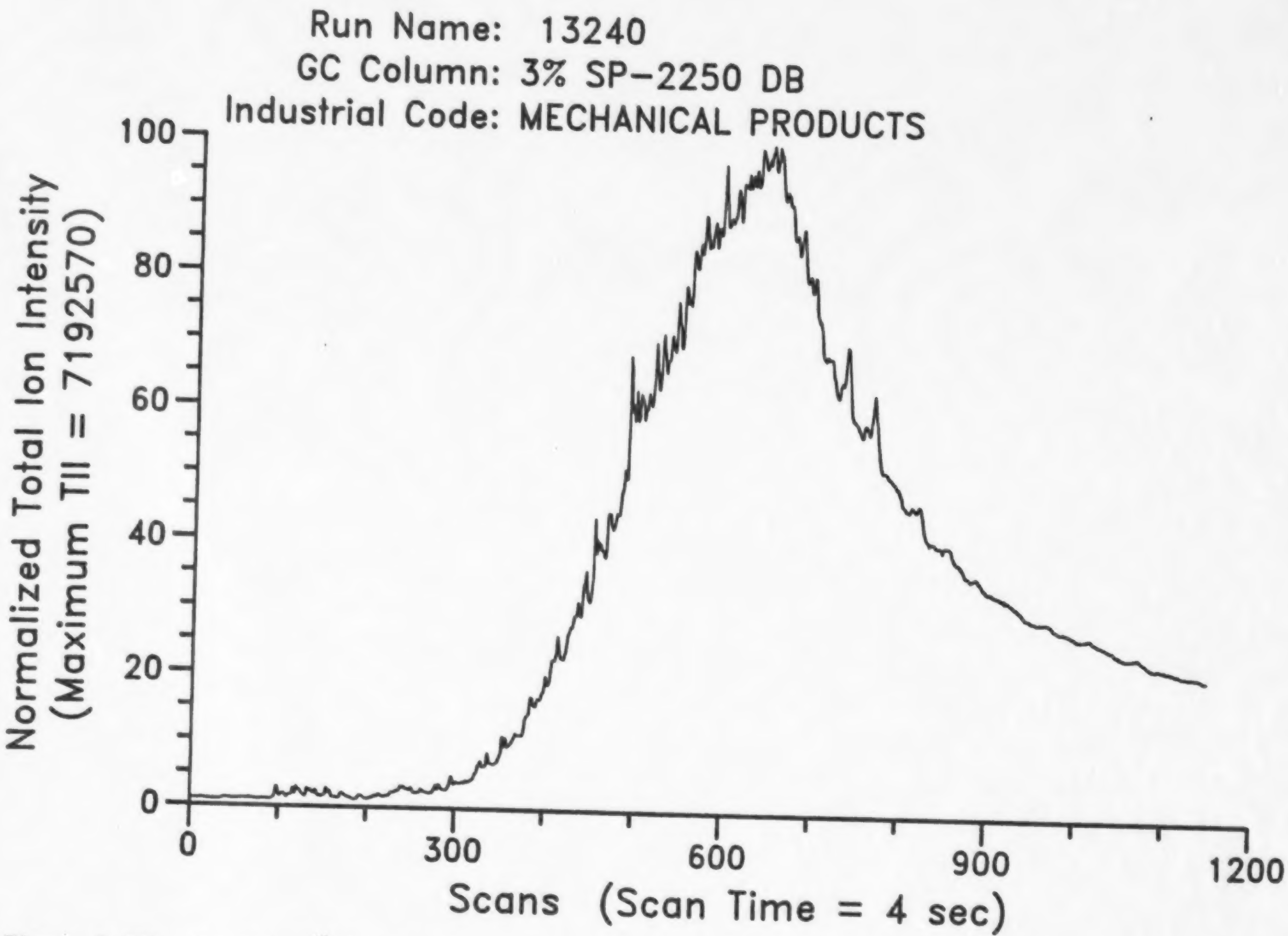


Figure 5.102. Packed column chromatogram, extract 13240 (base/neutral), mechanical products industry.

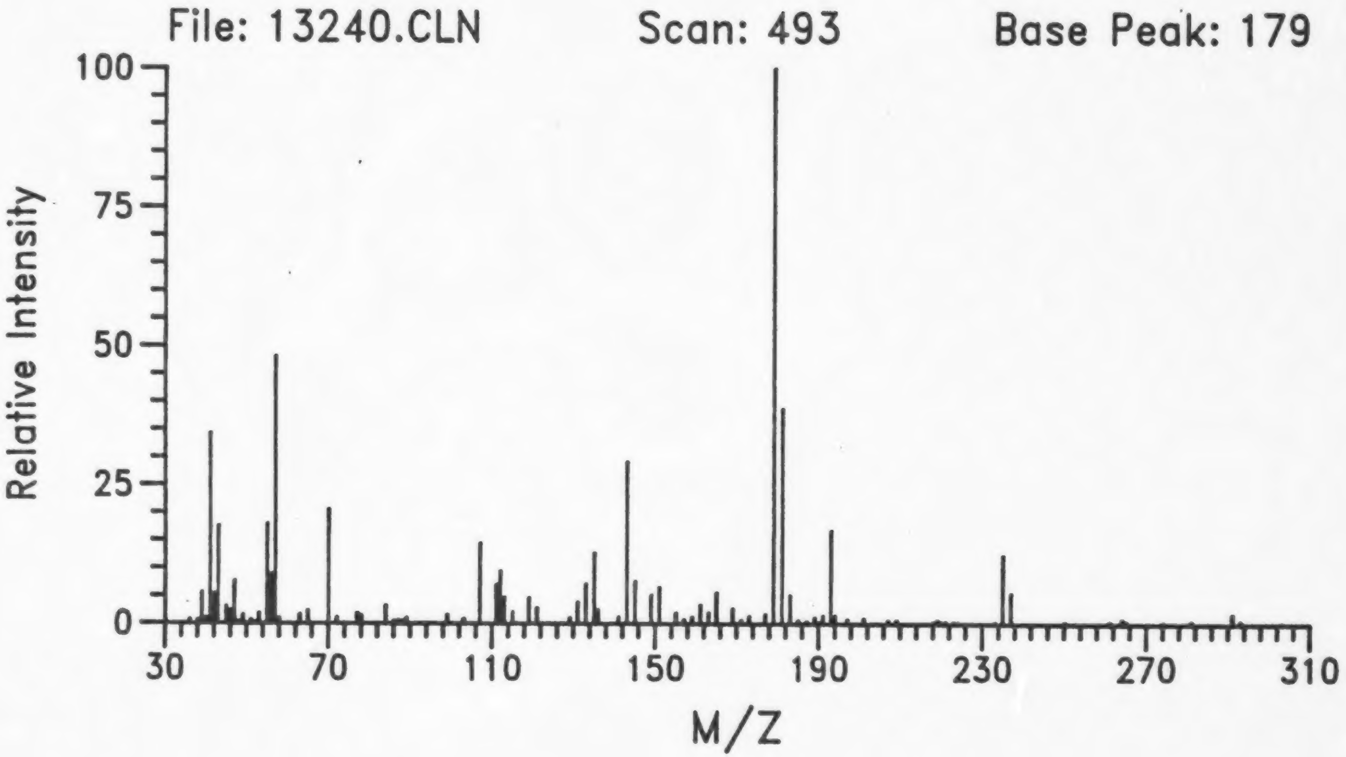


Figure 5.103. Extract 13240 (base/neutral), mechanical products industry. Frequency of occurrence: 5.

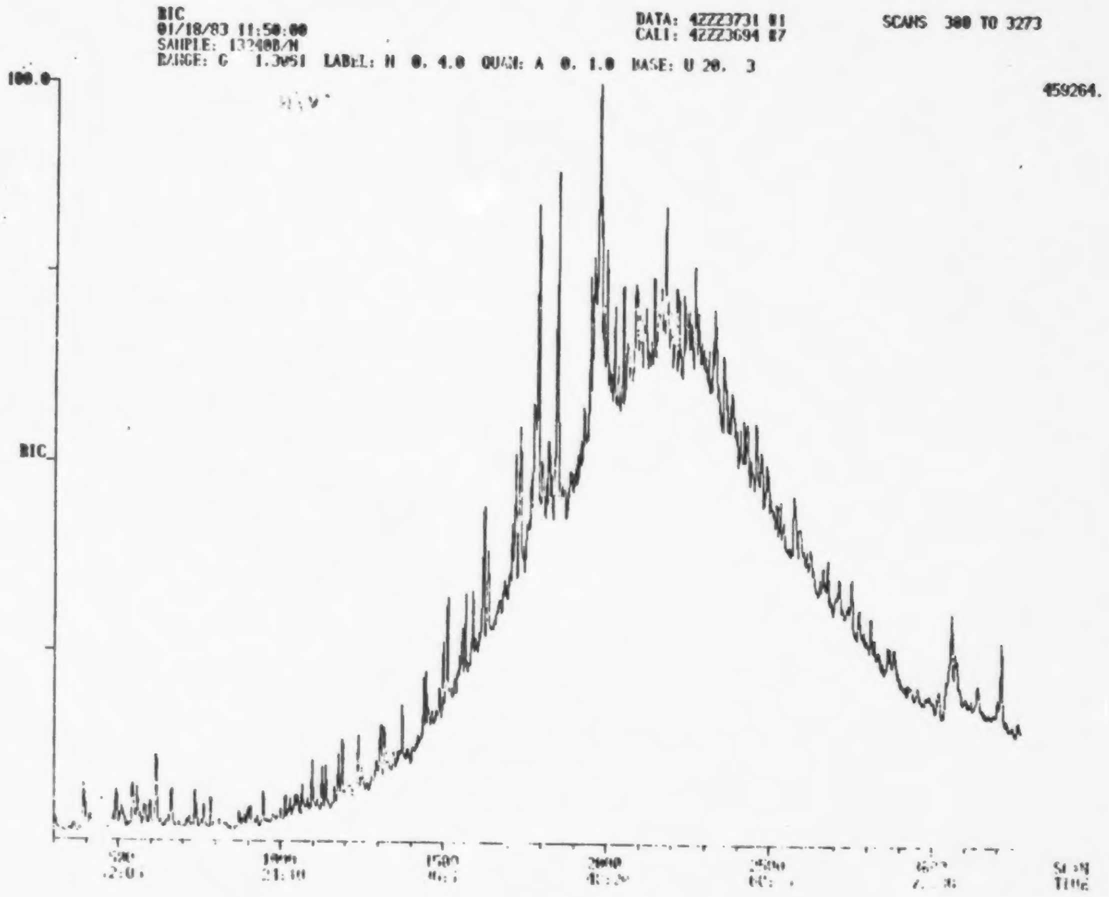


Figure 5.104. Capillary chromatogram of extract 13240 (base/neutral), mechanical products industry.

mass spectrum of the compound of interest are presented in Figures 5.105 and 5.106. These spectra correspond to the spectra obtained for extract 13230 (acid), also from the Mechanical Products Industry. When extract 13240 was fractionated (Figures 5.107-5.109), a family of seven spectra obviously related to the mass spectrum of the compound of interest was observed (Figures 5.110-5.117), although an exact match of spectra was not obtained after fractionation. All of these clean mass spectra could not be observed without the fractionation. The major differences in the mass spectra appear to be in the relative abundances of the low mass peaks, those corresponding to the hydrocarbon ions. It seems that at least six to seven of the carbon atoms are grouped together and are arranged differently (*i.e.*, different branching, etc.) for the compounds which produce the different mass spectra. The molecule obviously contains a hydrocarbon chain, phosphorus bonded to oxygen, chlorine, and probably sulfur. Structural information from FT-IR would be extremely valuable in making further structure assignments, but the concentration of the components of interest was not high enough.

Extract 13248 (Base/Neutral), Mechanical Products Industry, Influent to Coolant

The packed column chromatogram of extract 13248 (base/neutral) is shown in Figure 5.118. The mass spectrum of the compound of interest is presented in Figure 5.119. The capillary chromatogram of extract 13248 is shown in Figure 5.120. An extracted ion current profile shows that several members of a family of related compounds are seen in this extract (Figure 5.121). The mass spectra of six of these compounds are shown in Figures 5.122-5.127. When the extract is fractionated (Figures 5.128-5.130), mass spectra of this family of compounds are seen in fraction 2 (Figures 5.131-5.134). The mass spectra are obviously very closely related to the mass spectra observed in extract 13230 (acid) and 13240 (base/neutral). although m/z 235 is no longer observed. Accurate mass measurement produces the same list of possibilities. Chemical ionization mass spectrometry, positive and negative modes, shows that the highest mass ion observed under electron ionization is not the molecular ion: ions are observed in the same spectra as the characteristic 179/181

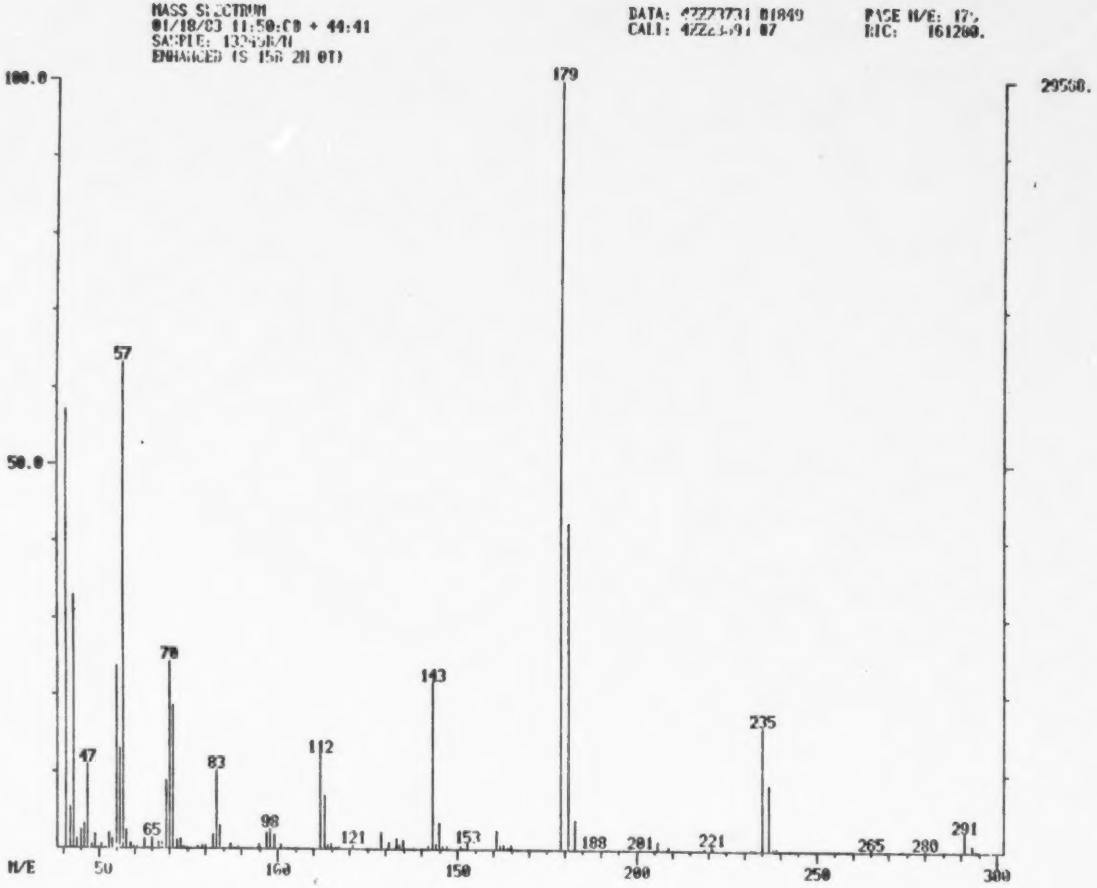


Figure 5.105. Mass spectrum of EPA compound of interest, extract 13240 (base/neutral), mechanical products industry, scan #1849.

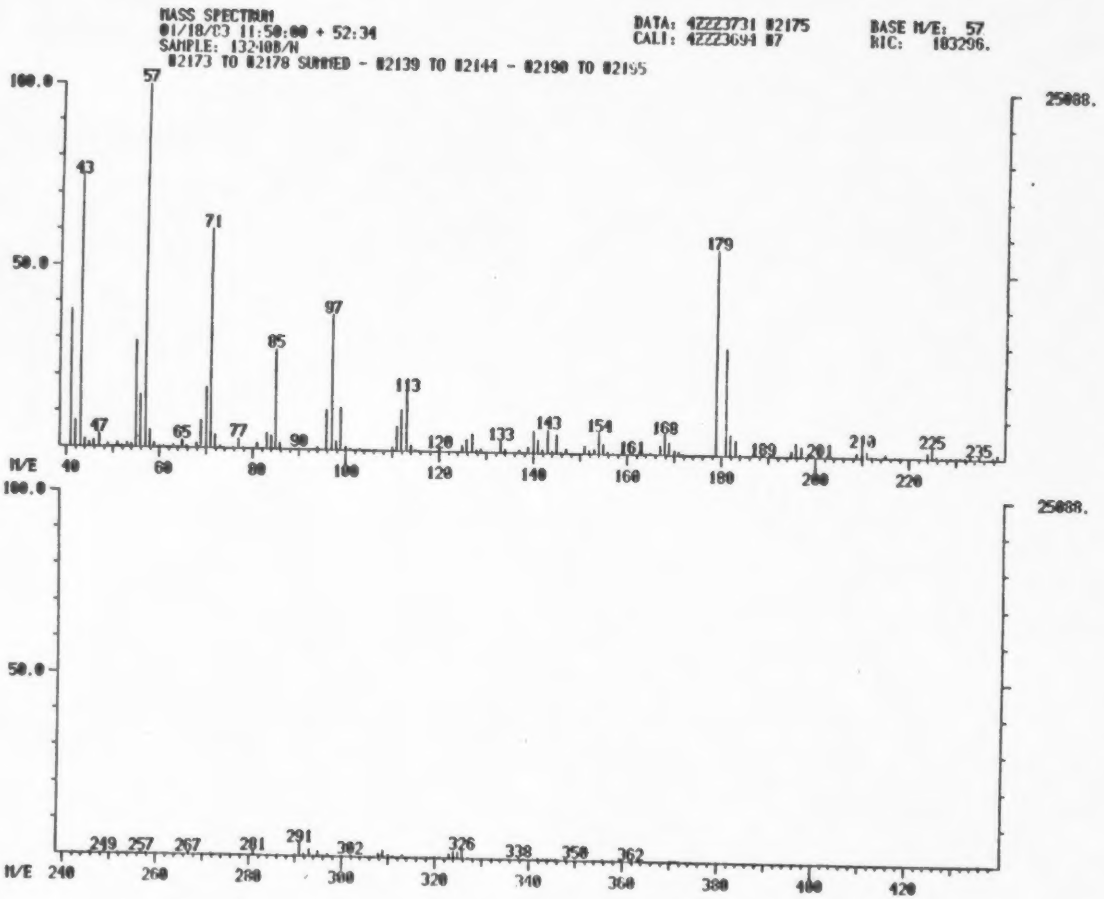


Figure 5.106. Mass spectrum of EPA compound of interest, extract 13240 (base/neutral), mechanical products industry, scan #2175.

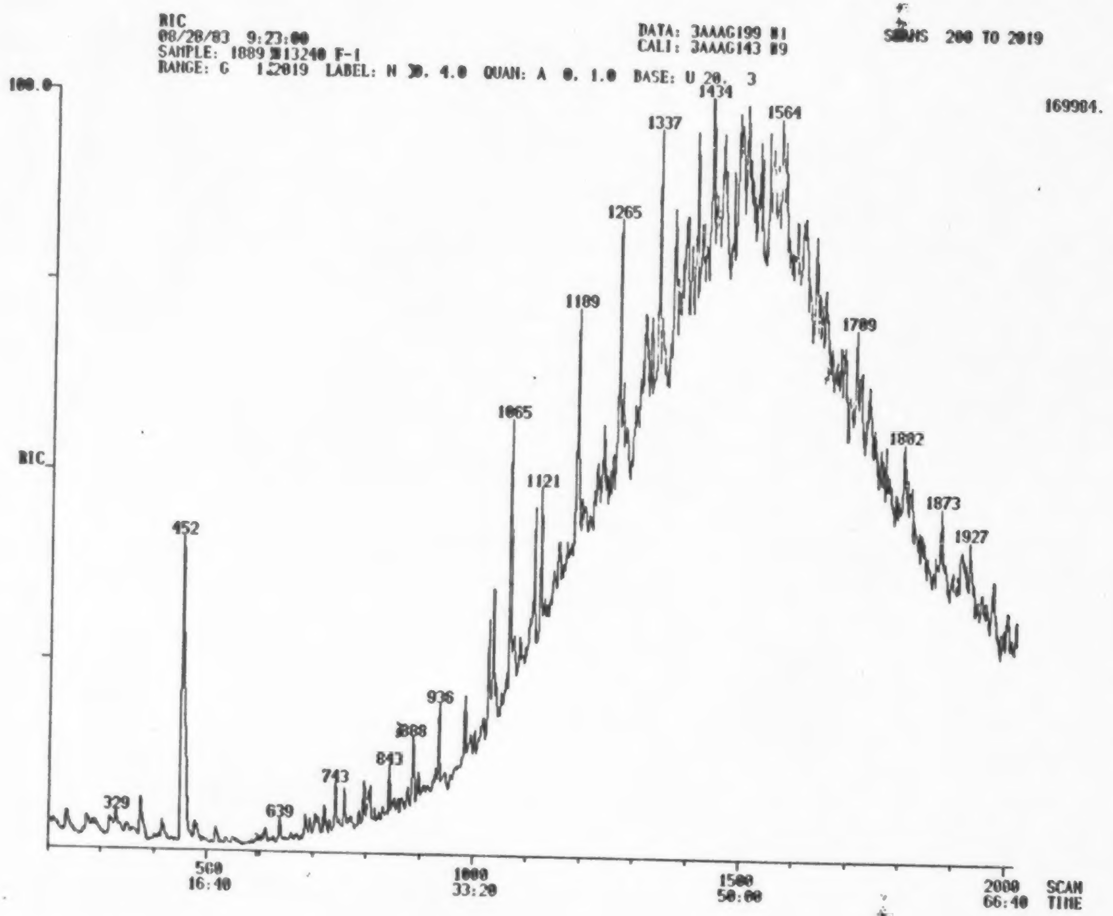


Figure 5.107. Capillary chromatogram of extract 13240 (base/neutral), fraction 1.

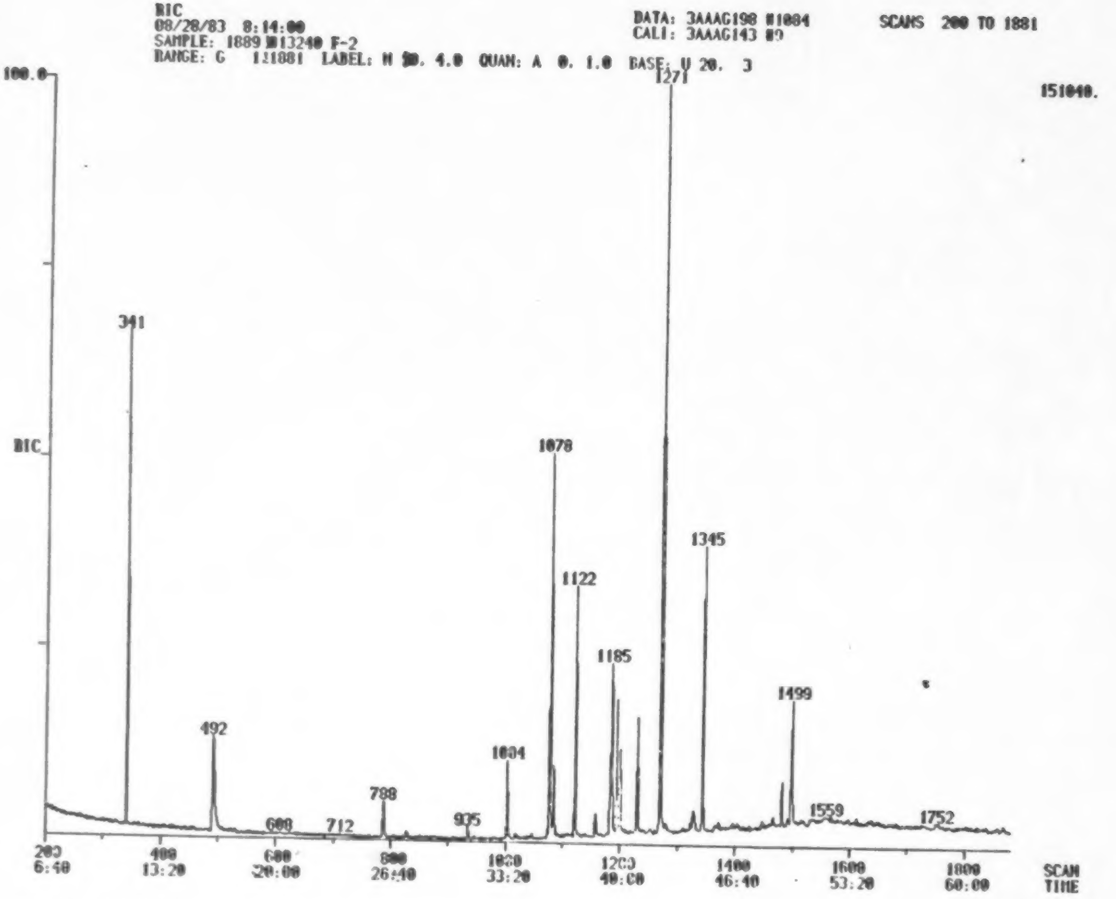


Figure 5.108. Capillary chromatogram of extract 13240 (base/neutral), fraction 2.

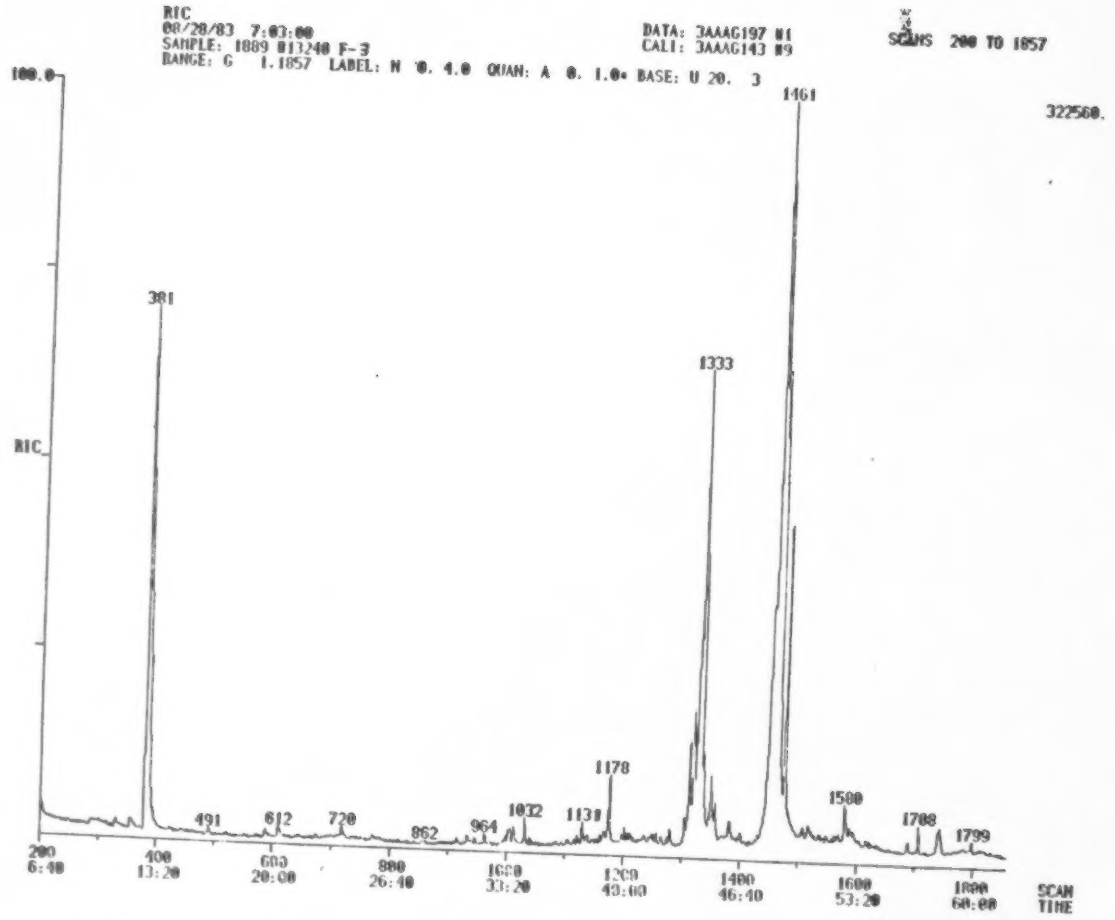


Figure 5.109. Capillary chromatogram of extract 13240 (base/neutral), fraction 3.

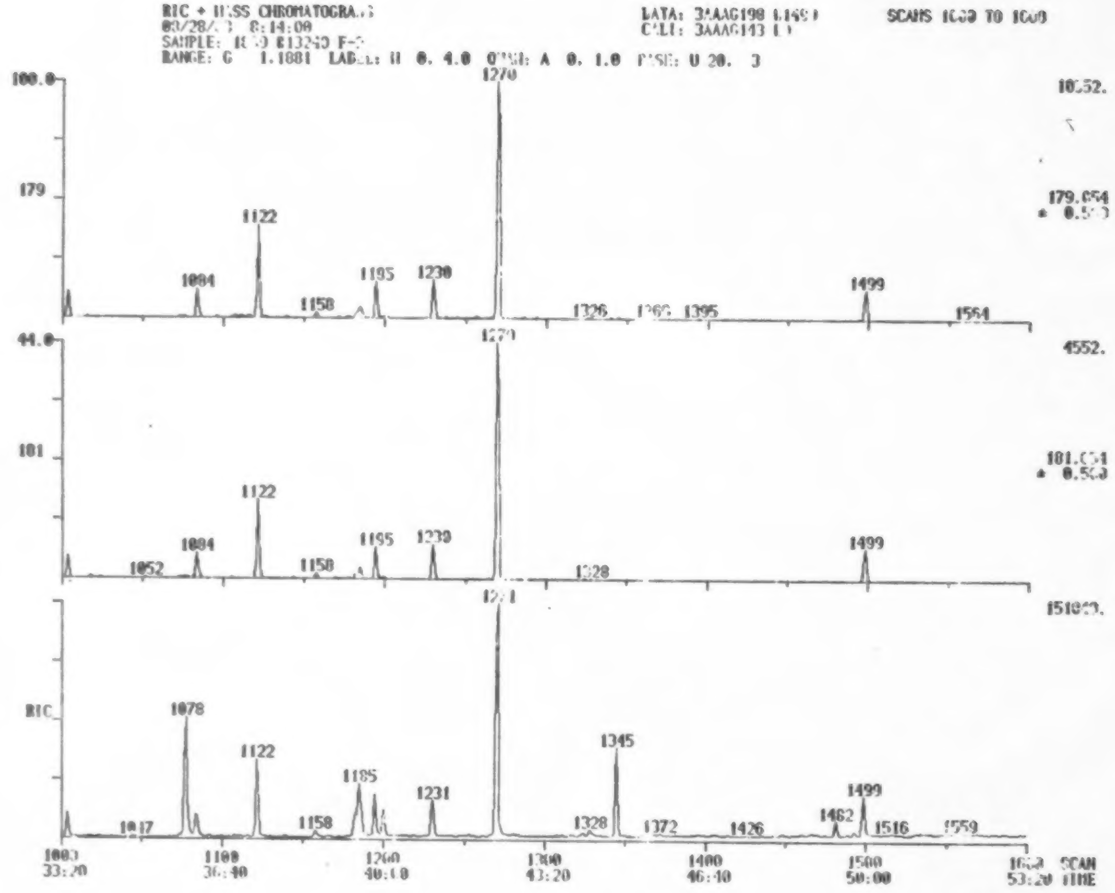


Figure 5.110. Extracted ion current profile, m/z 179, 181, in fraction 2.

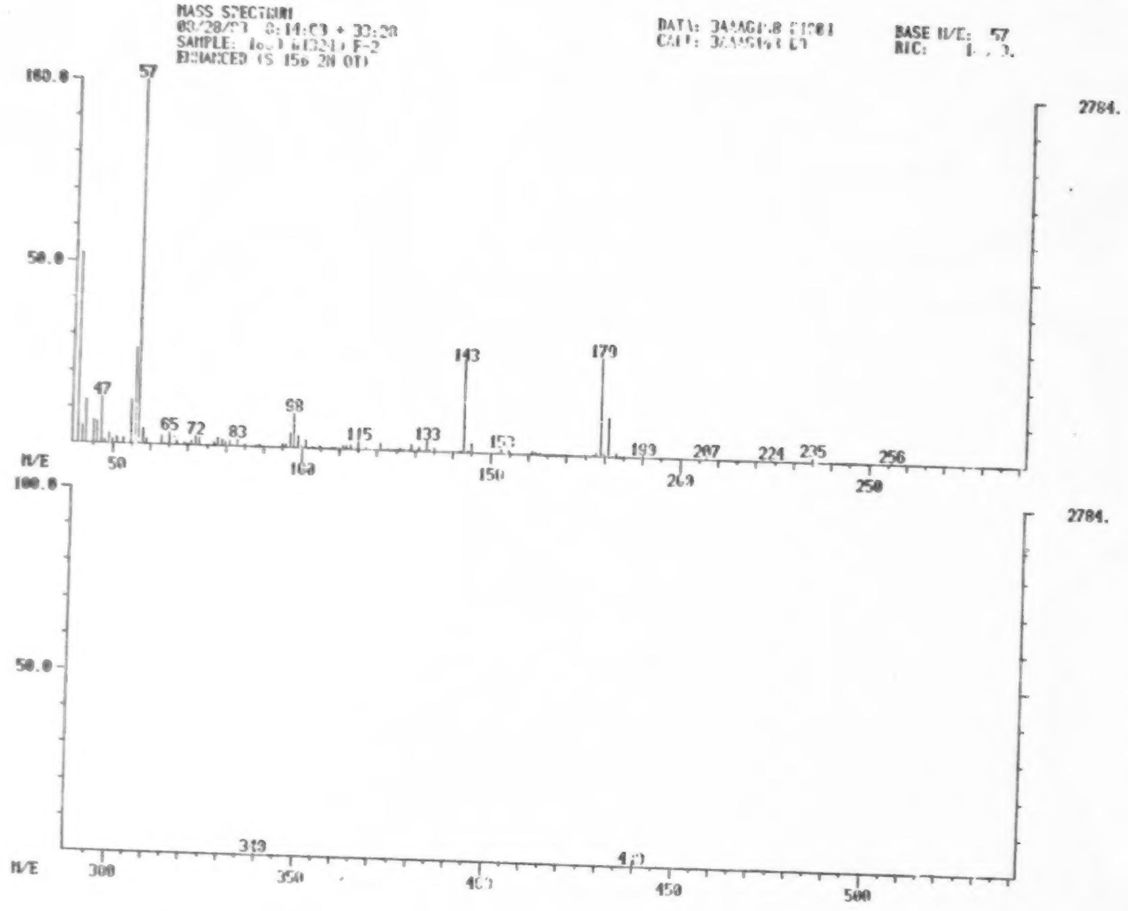


Figure 5.111. Mass spectrum of EPA compound of interest, scan #1004.

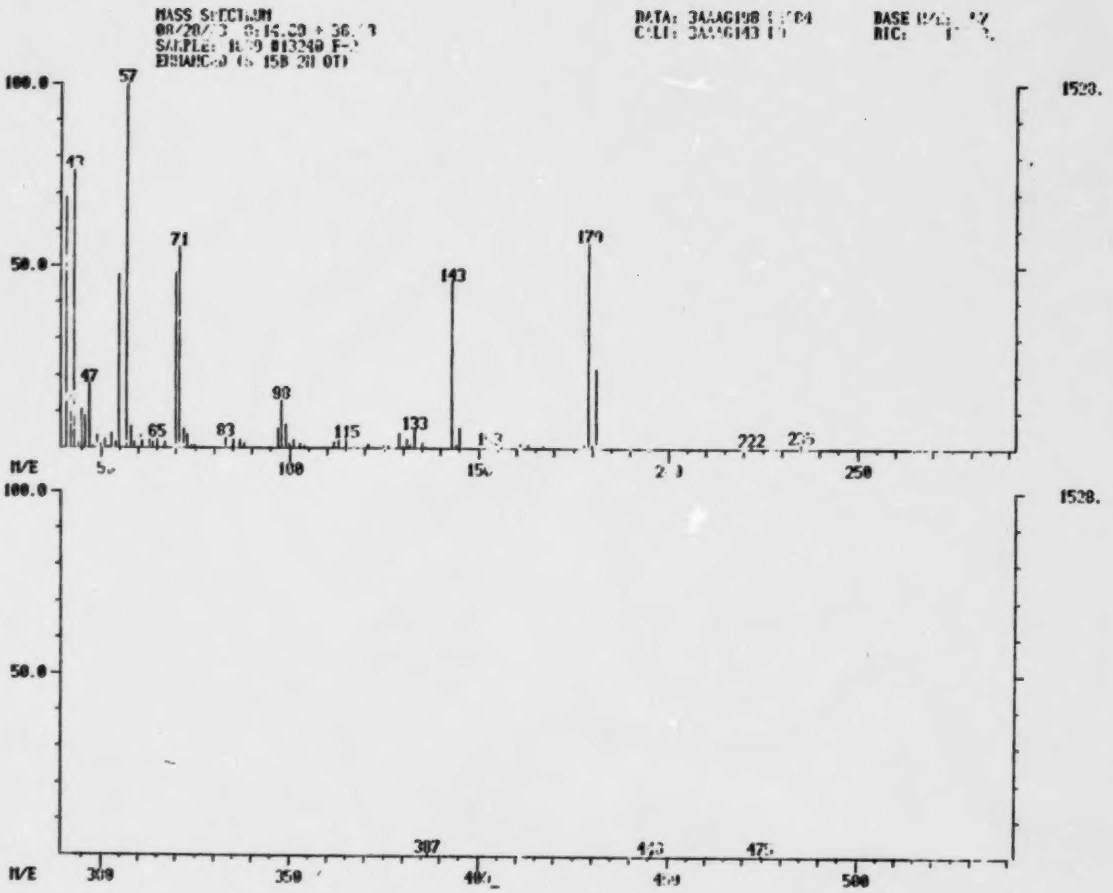


Figure 5.112. Mass spectrum of EPA compound of interest, scan #1084.

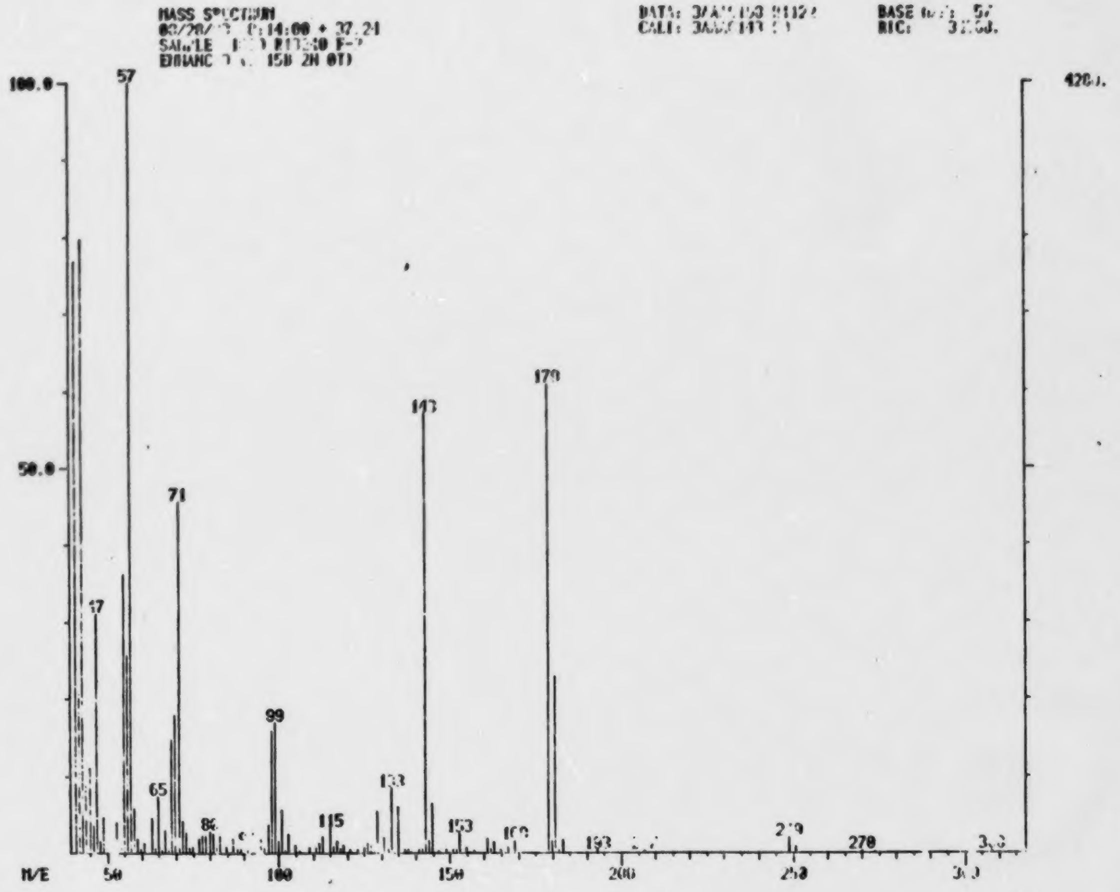


Figure 5.113. Mass spectrum of EPA compound of interest, scan #1122.

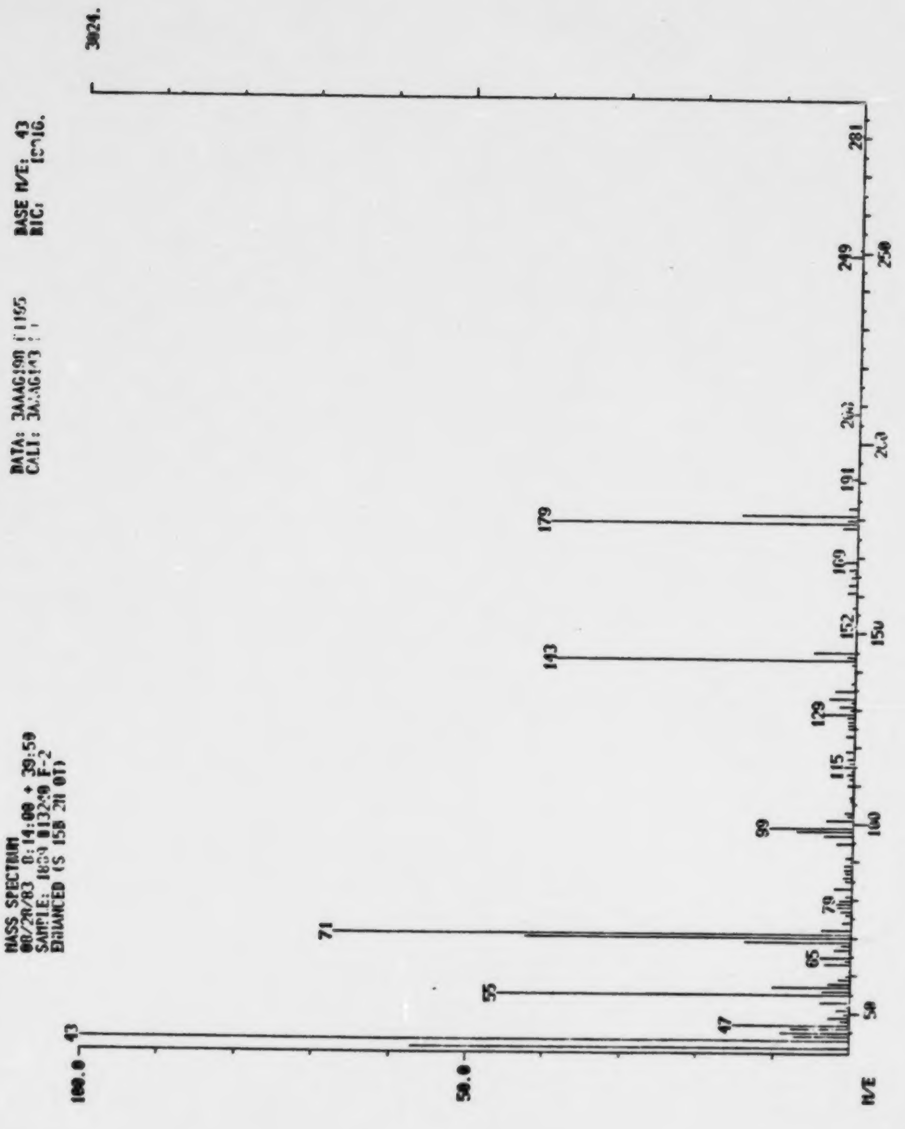


Figure 5.114. Mass spectrum of EPA compound of interest, scan #1195.

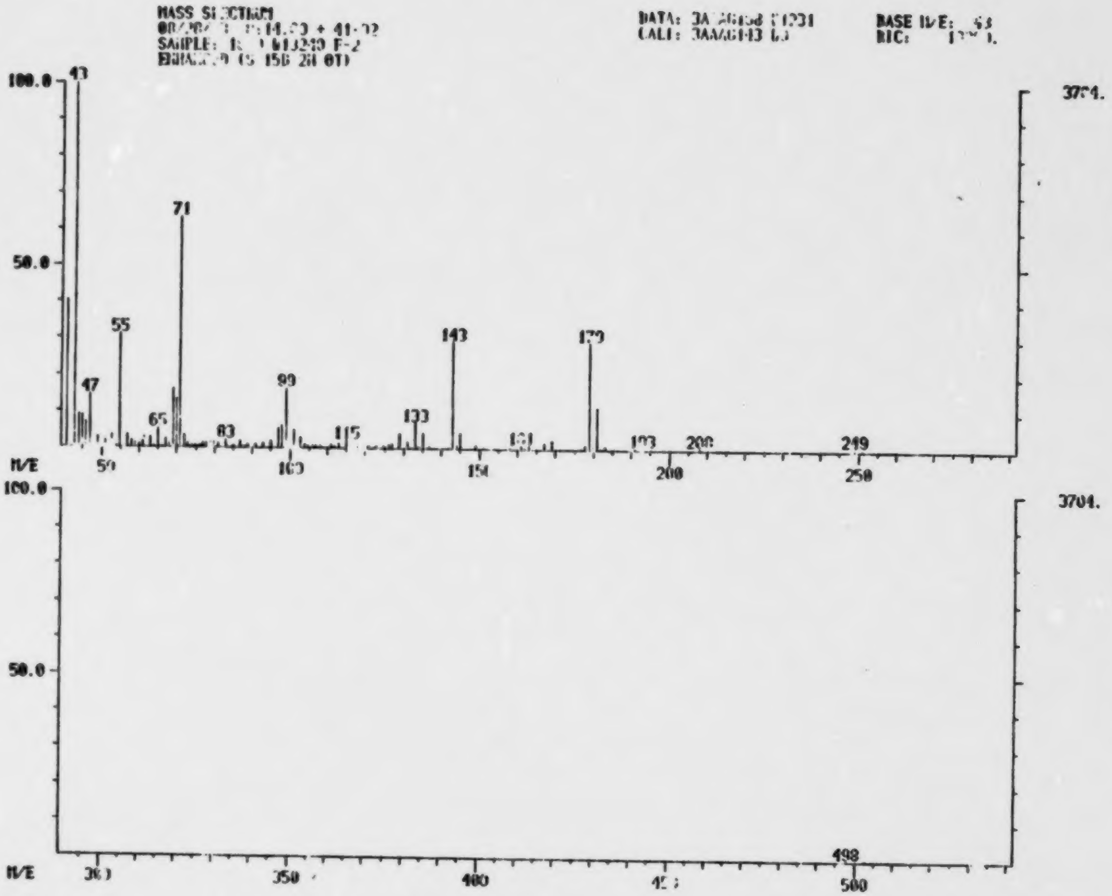


Figure 5.115. Mass spectrum of EPA compound of interest, scan #1231.

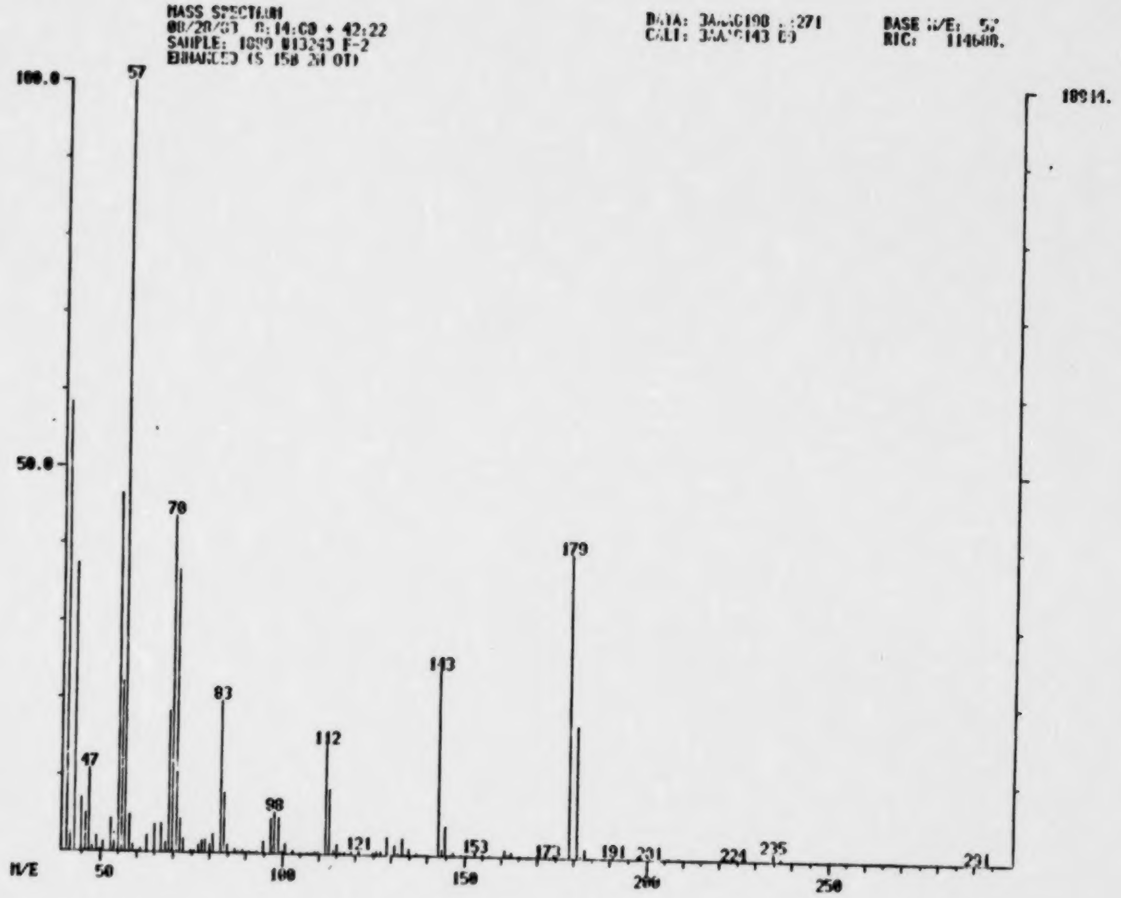


Figure 5.116. Mass spectrum of EPA compound of interest, scan #1271.

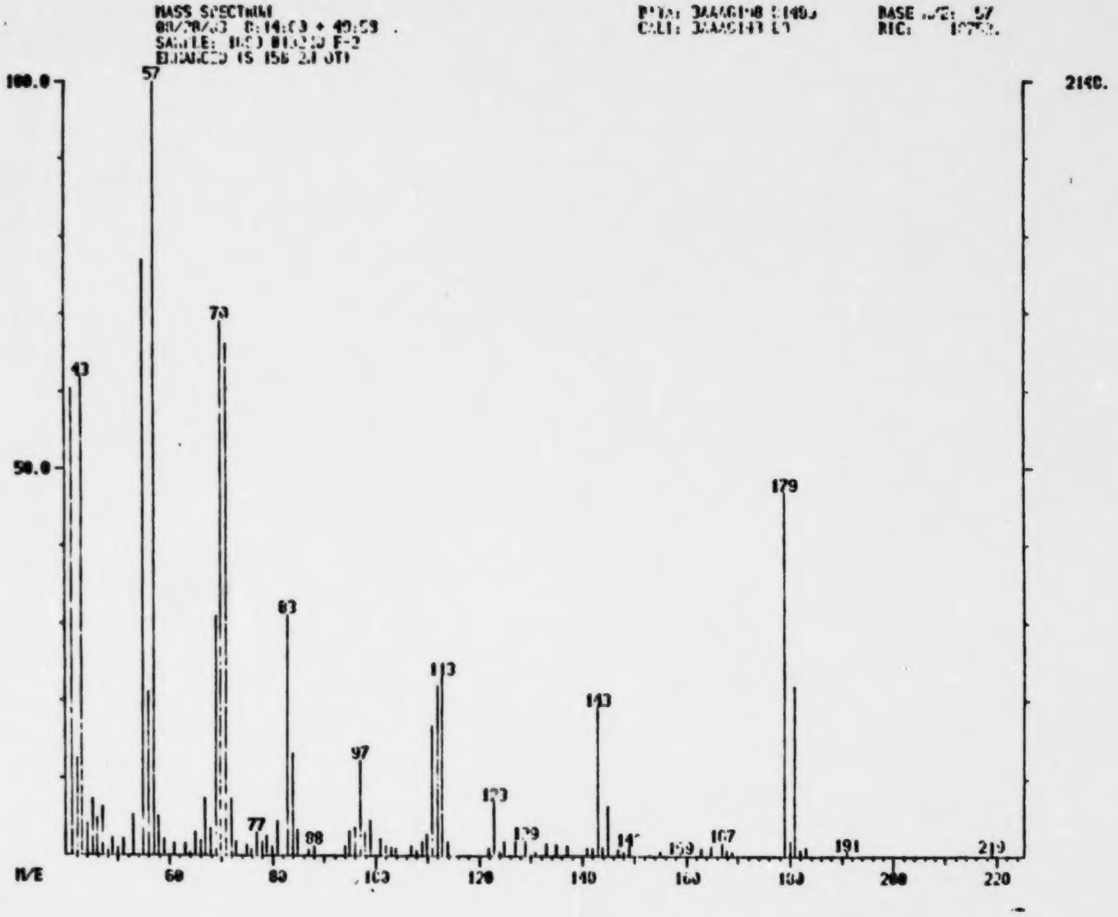


Figure 5.117. Mass spectrum of EPA compound of interest, scan #1499.

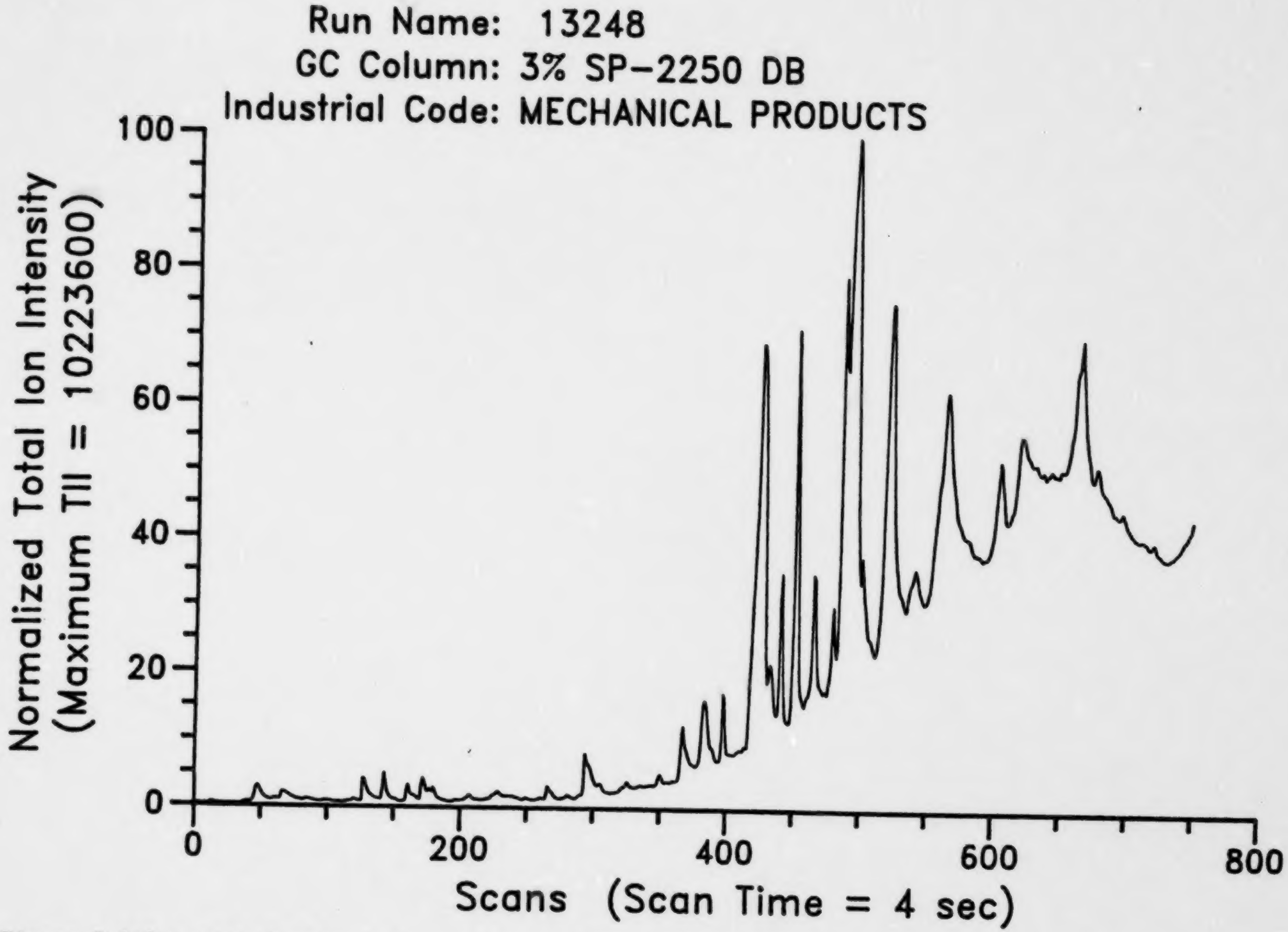


Figure 5.118. Packed column chromatogram, extract 13248 (base/neutral), mechanical products industry.

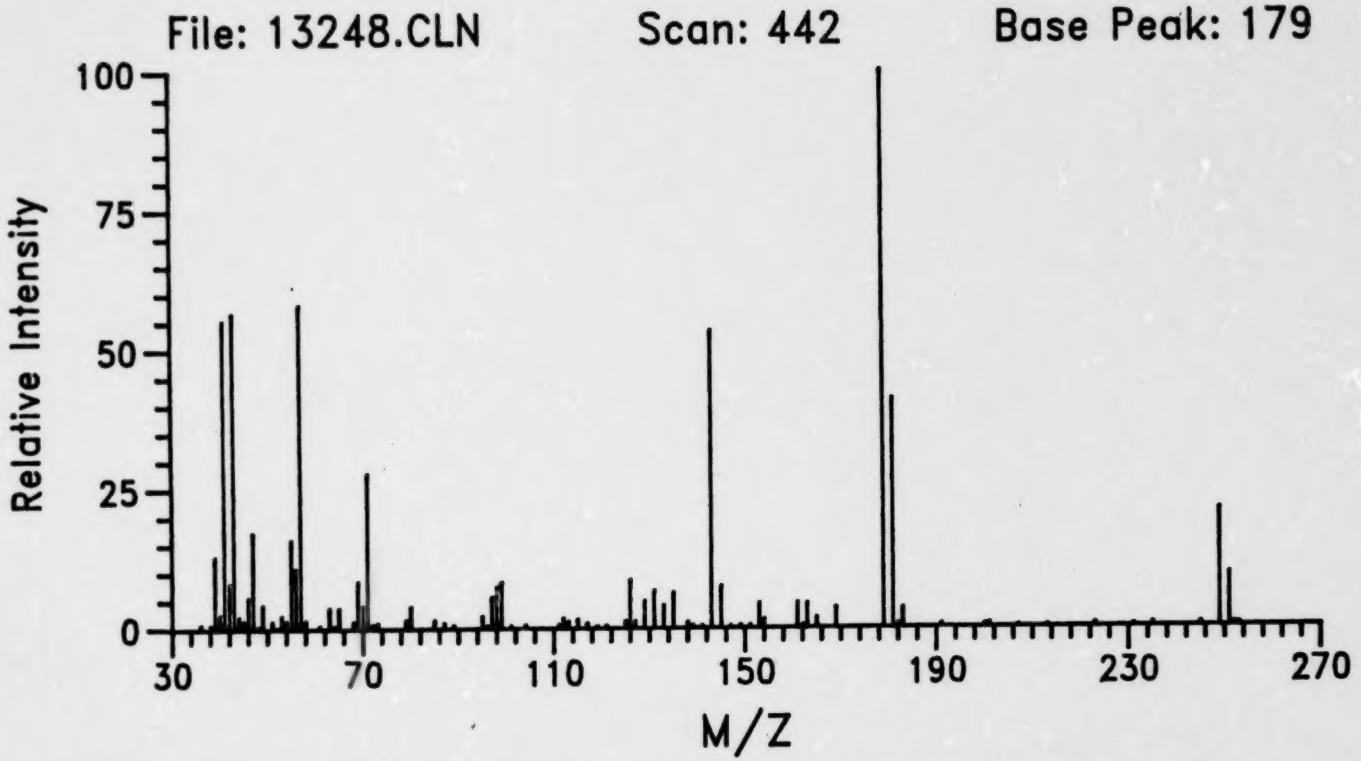


Figure 5.119. Extract 13248 (base/neutral), mechanical products industry. Frequency of occurrence: 15.

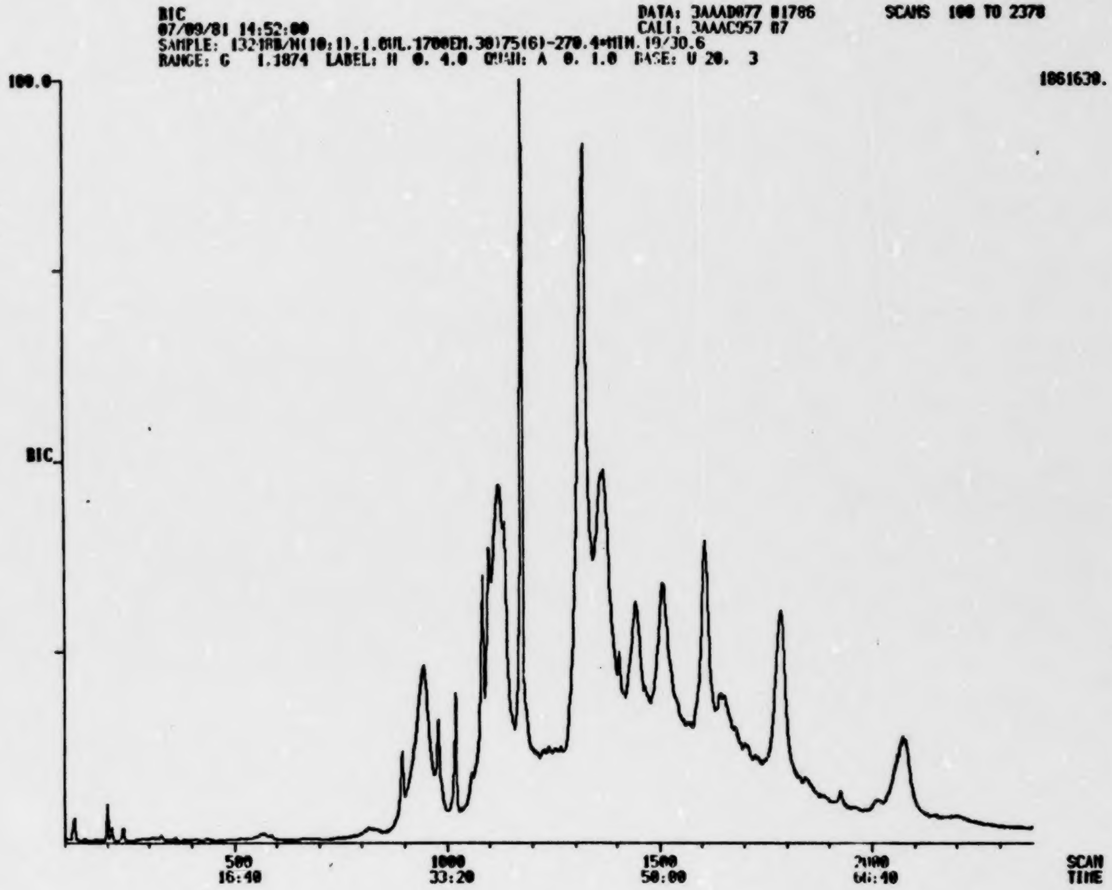


Figure 5.120. Capillary chromatogram of extract 13248 (base/neutral), mechanical products industry.

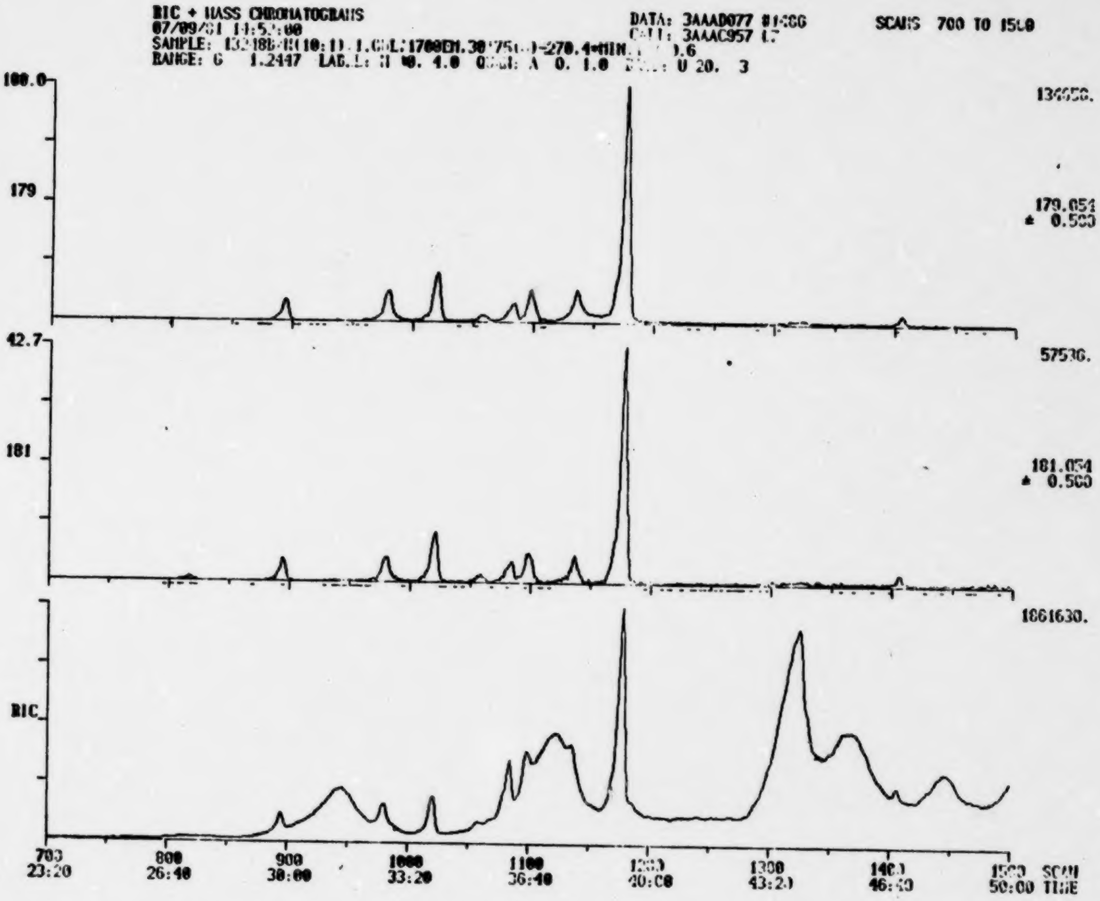


Figure 5.121. Extracted ion current profile, m/z 179 and 181.

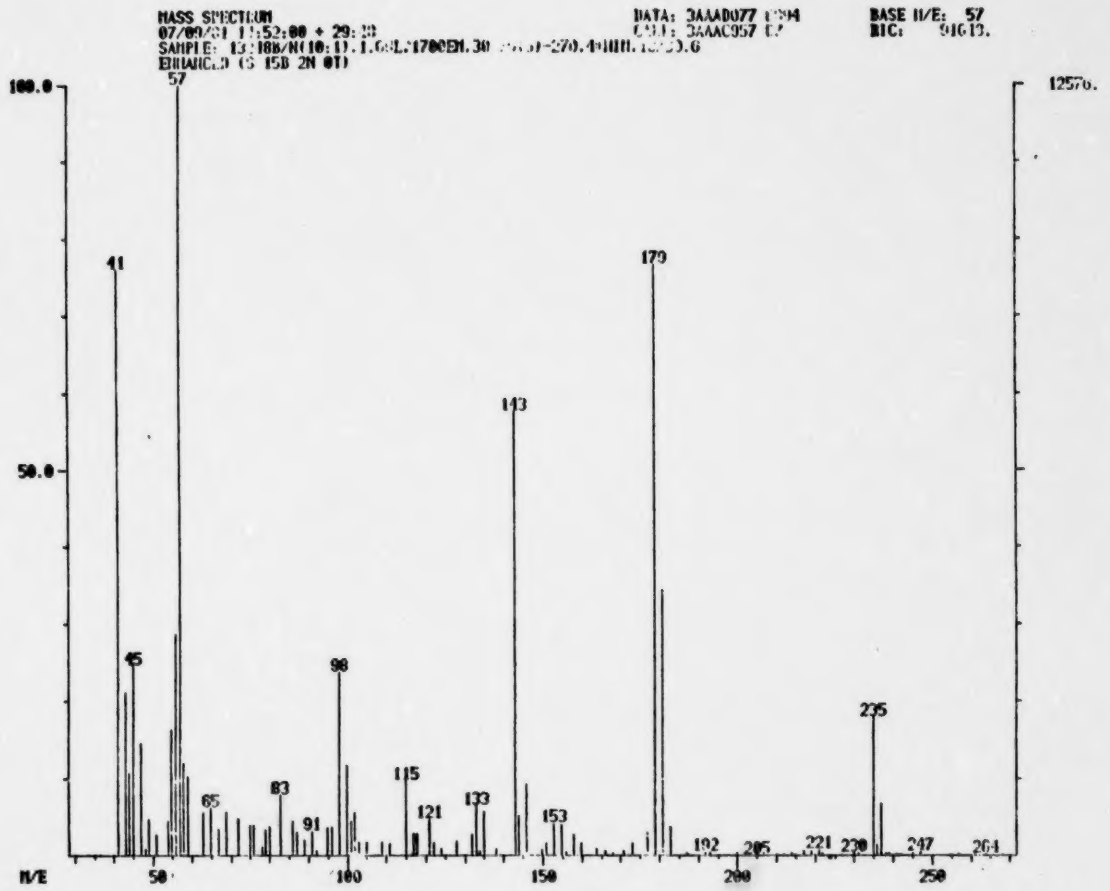


Figure 5.122. Mass spectrum of EPA compound of interest, extract 13248 (base/neutral), mechanical products industry, scan #894.

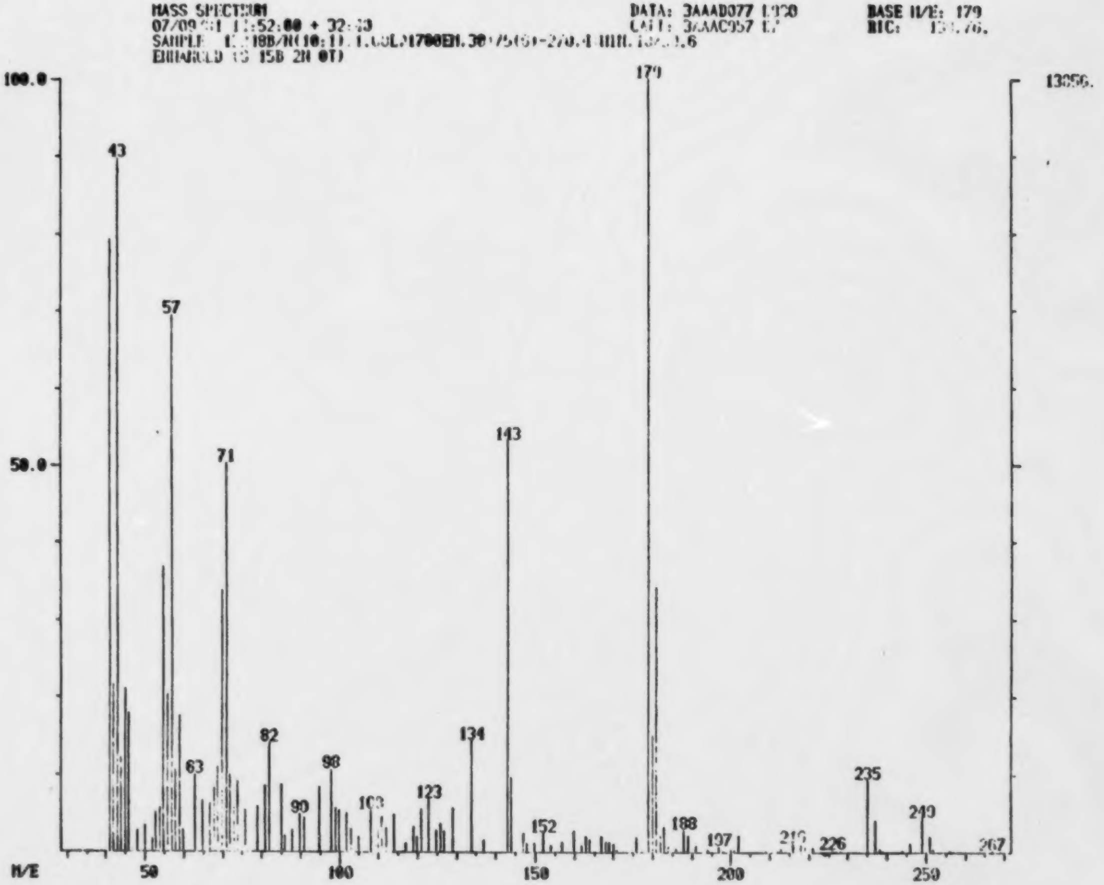


Figure 5.123. Mass spectrum of EPA compound of interest, extract 13248 (base/neutral), mechanical products industry., scan #980.

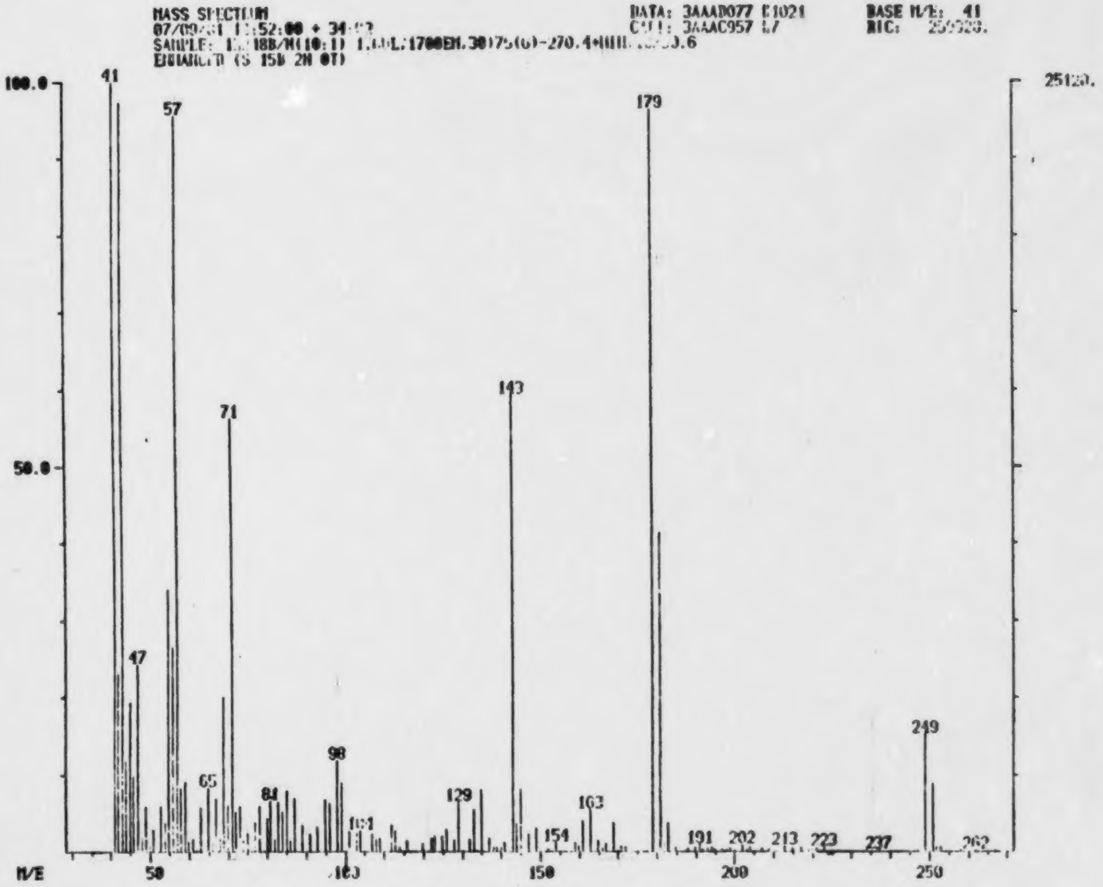


Figure 5.124. Mass spectrum of EPA compound of interest, extract 13248 (base/neutral), mechanical products industry , scan #1021.

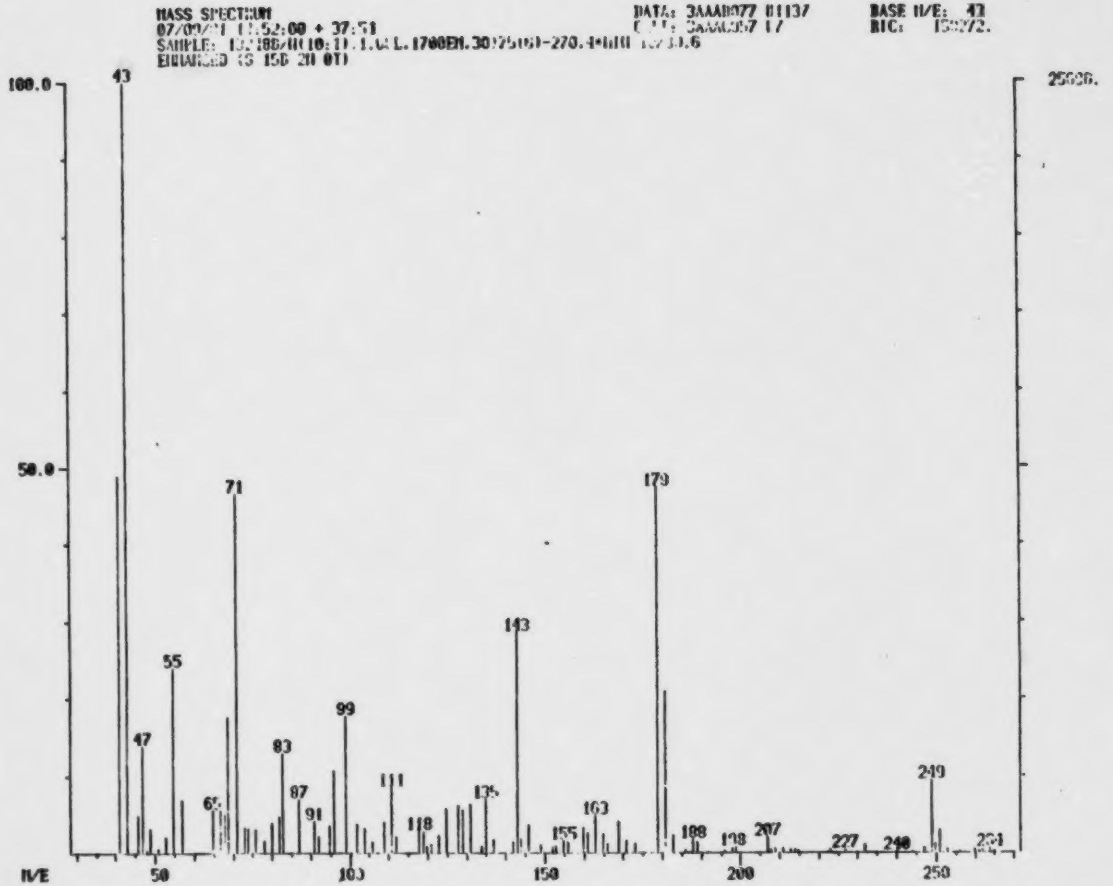


Figure 5.125. Mass spectrum of EPA compound of interest, extract 13248 (base/neutral), mechanical products industry, scan #1137.

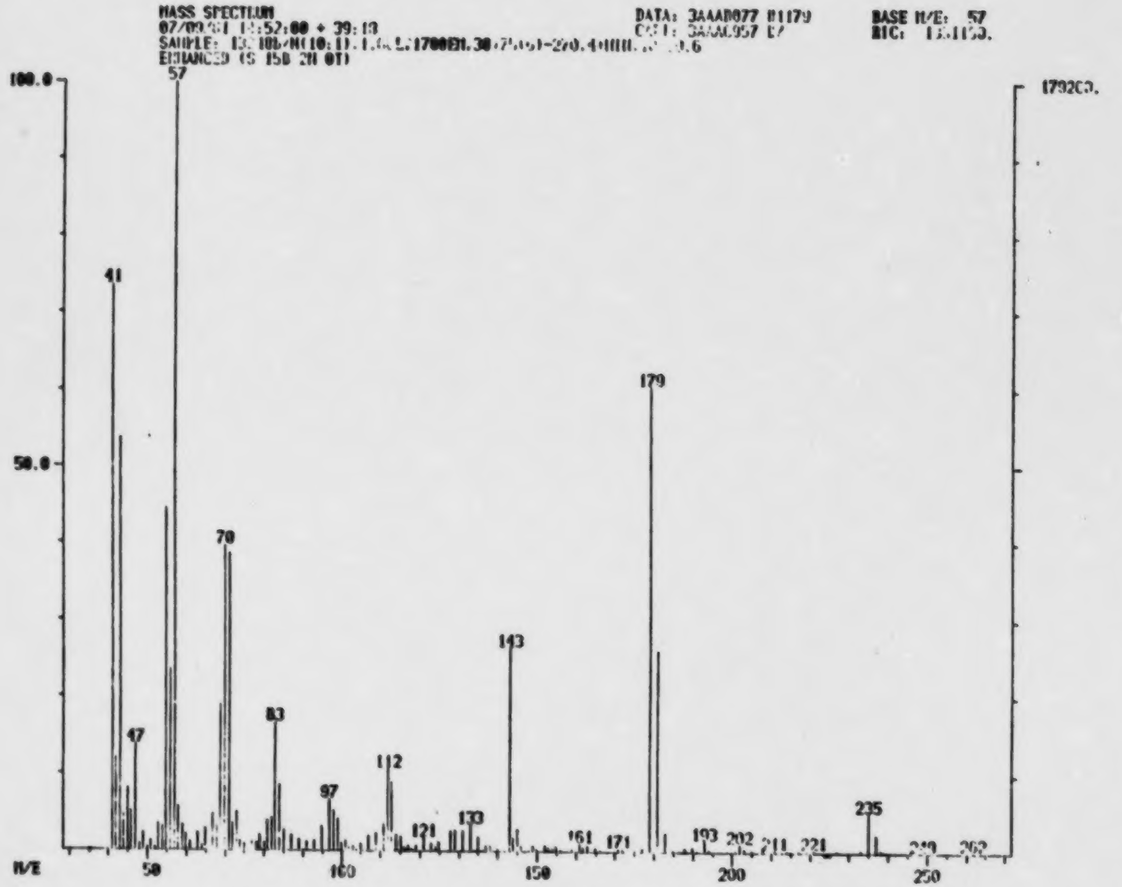


Figure 5.126. Mass spectrum of EPA compound of interest, extract 13248 (base/neutral), mechanical products industry, scan # 1179.

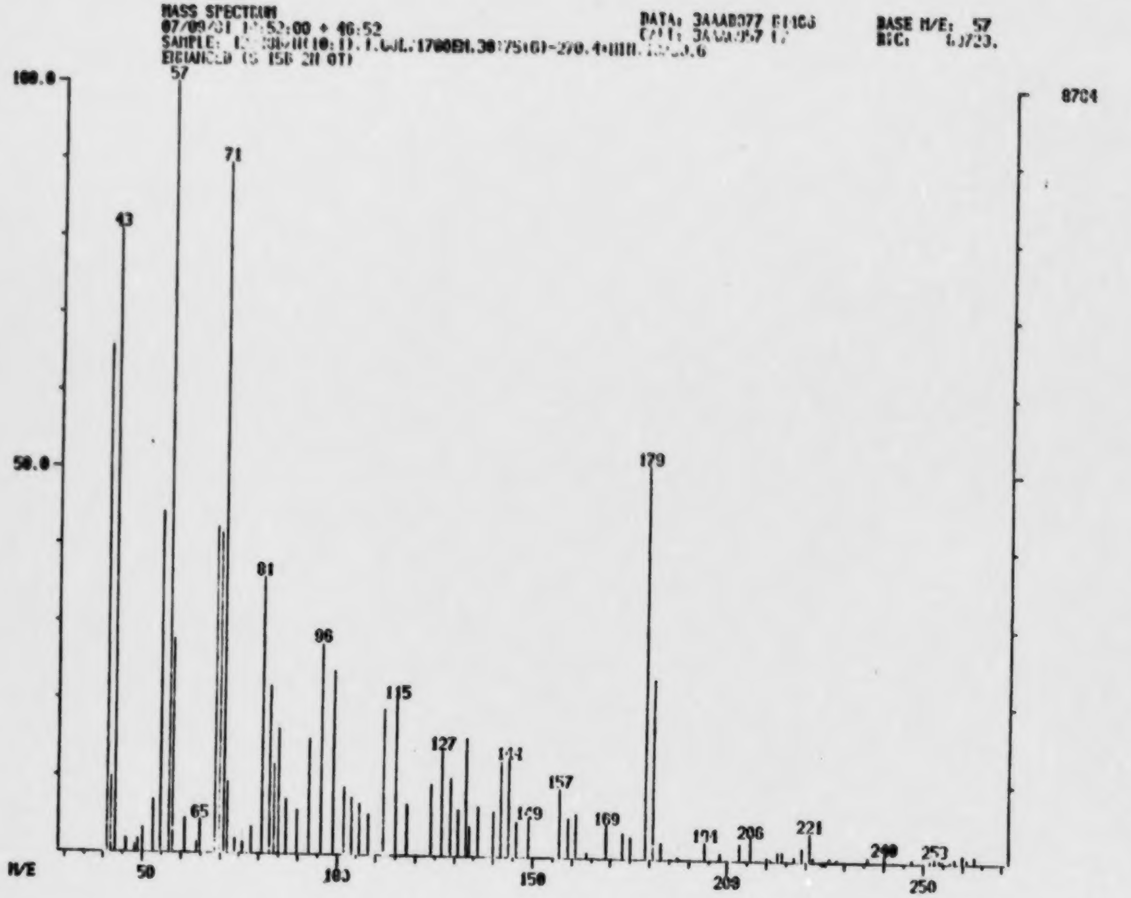


Figure 5.127. Mass spectrum of EPA compound of interest, extract 13248 (base/neutral), mechanical products industry , scan # 1466.

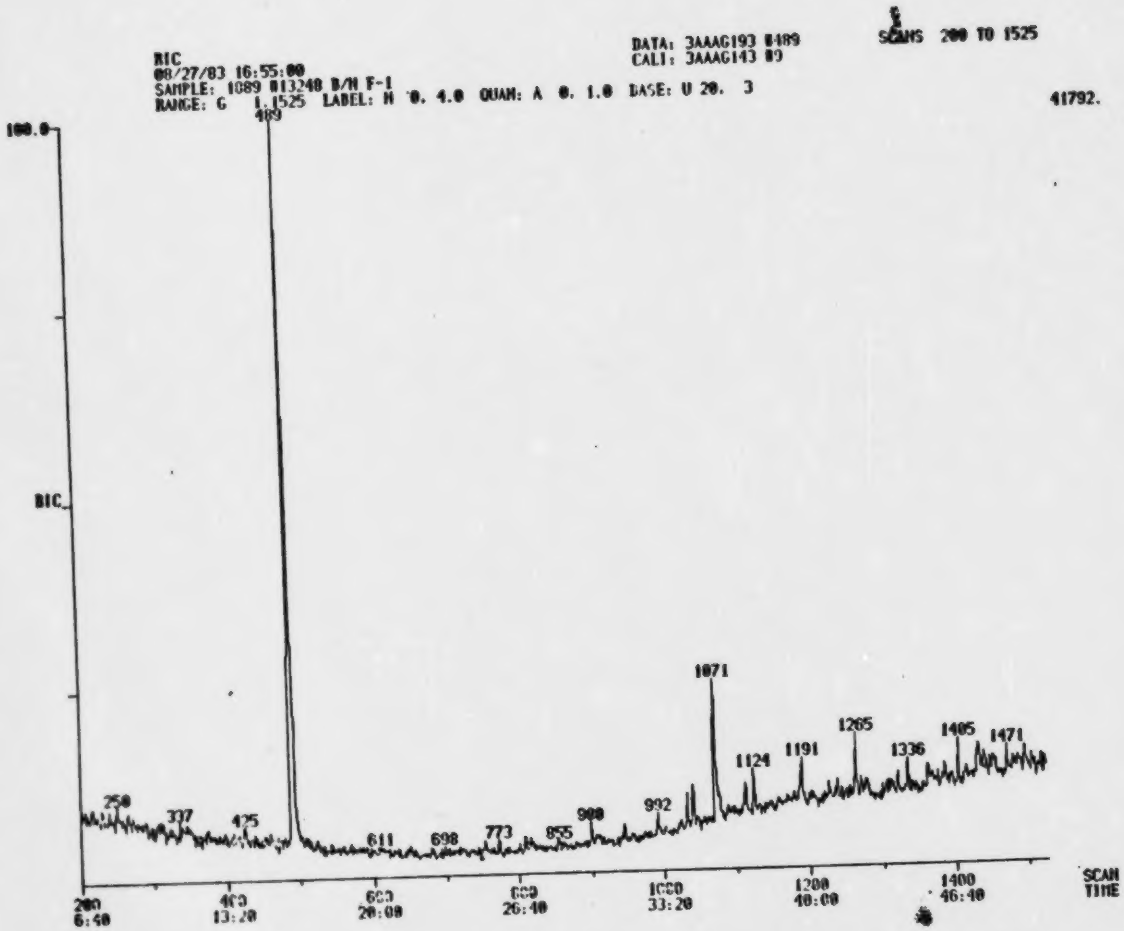


Figure 5.128. Capillary chromatogram of extract 13248 (base/neutral), fraction 1.

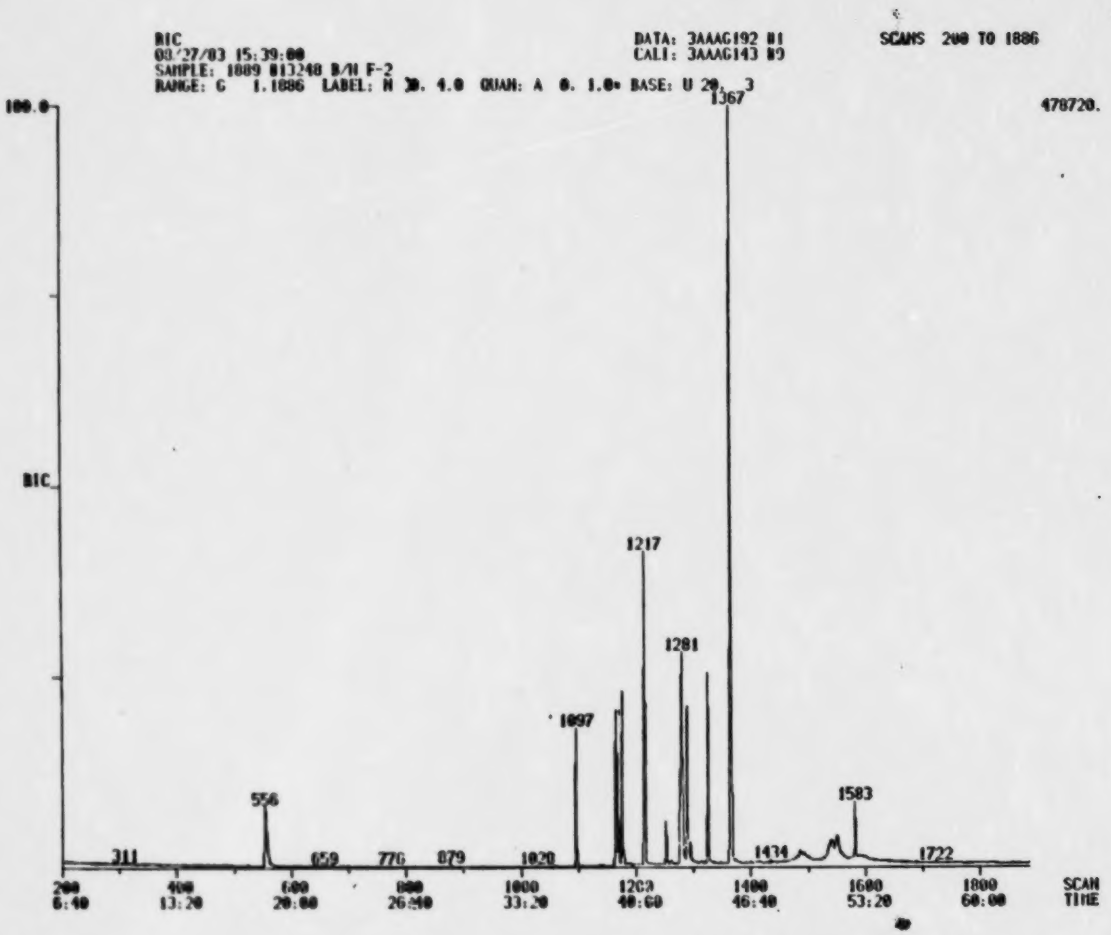


Figure 5.129. Capillary chromatogram of extract 13248 (base/neutral), fraction 2.

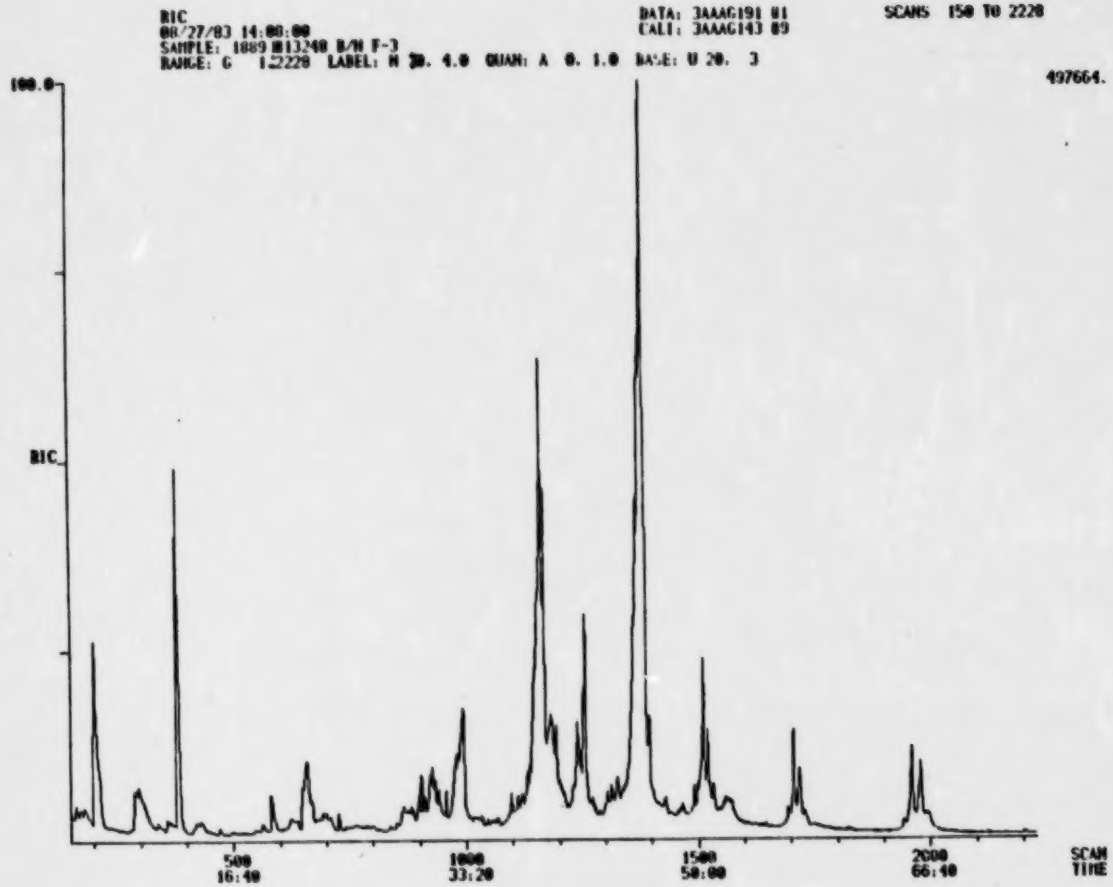


Figure 5.130. Capillary chromatogram of extract 13248 (base/neutral), fraction 3.

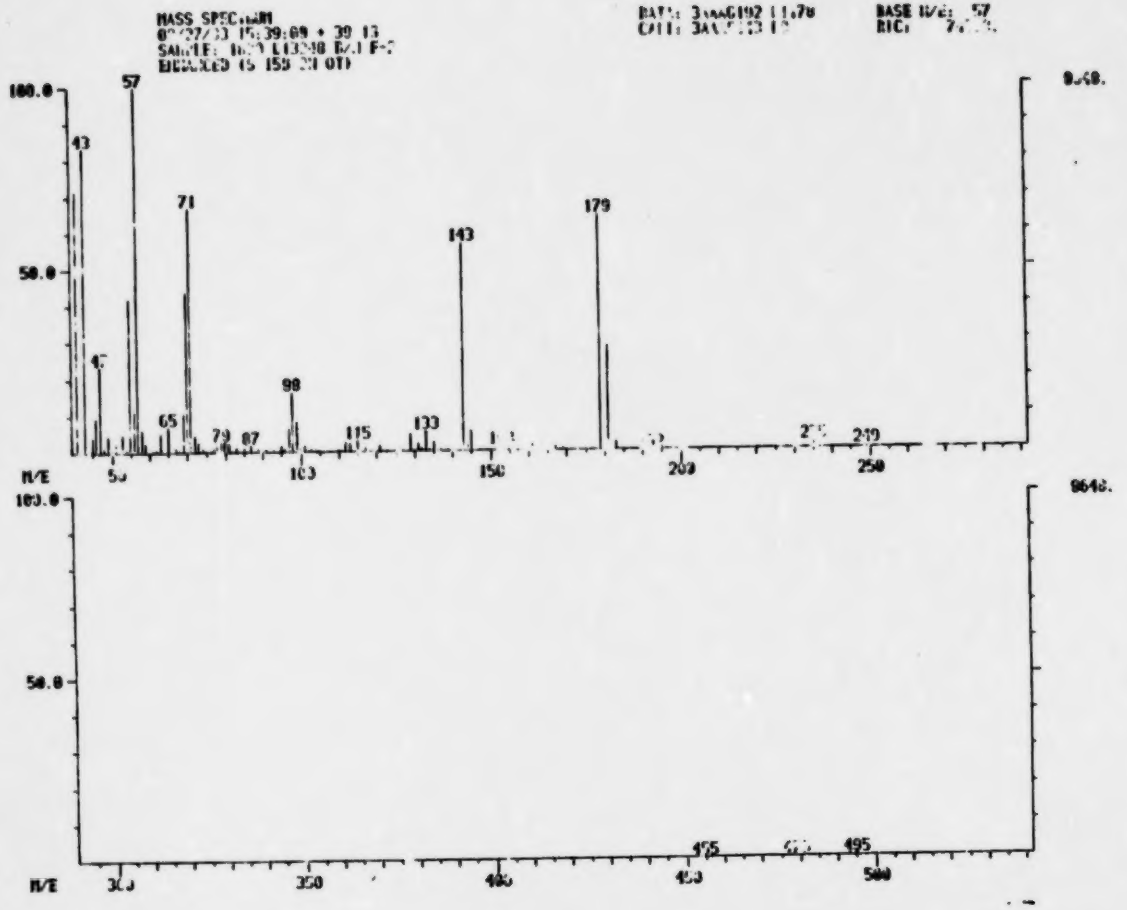


Figure 5.131. Mass spectrum of compound of interest, extract 13248 (base/neutral), fraction 2, scan #1178

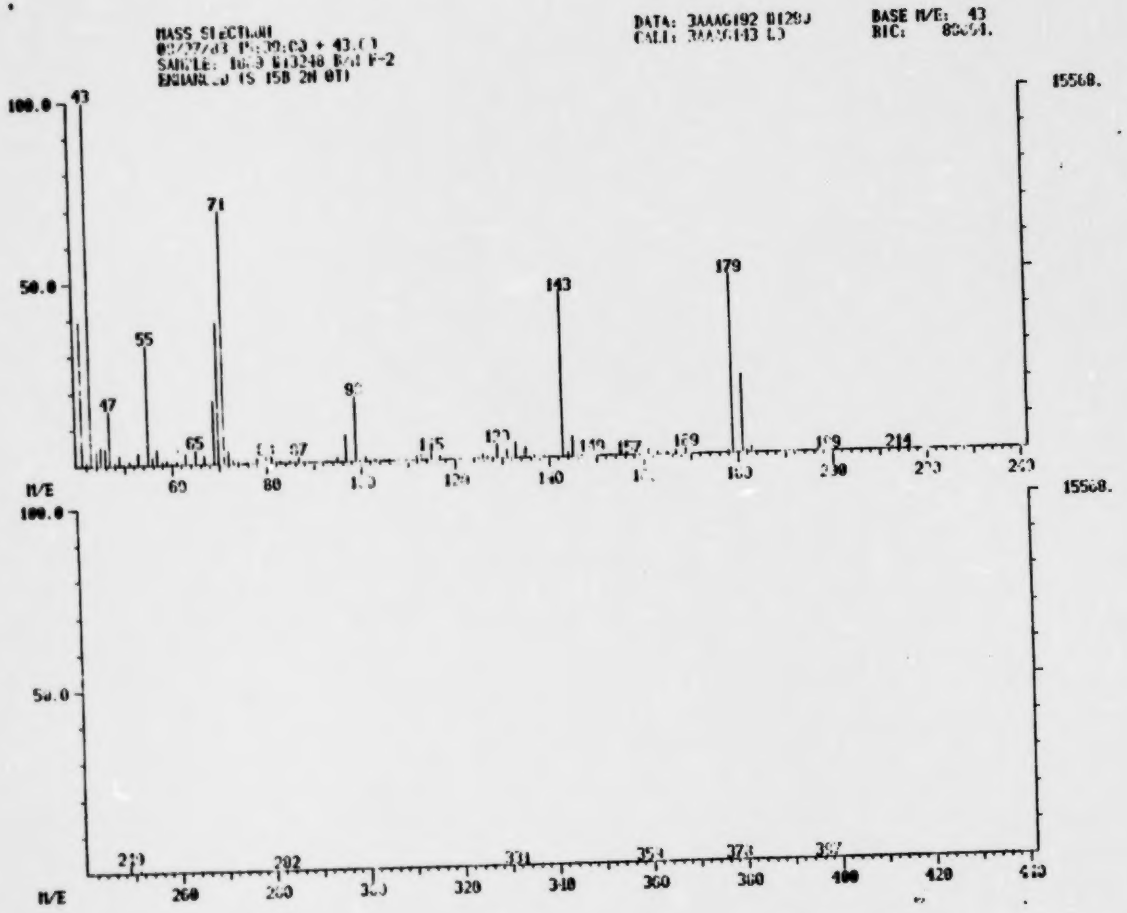


Figure 5.132. Mass spectrum of compound of interest, extract 13248 (base/neutral, fraction 2, scan #1290.

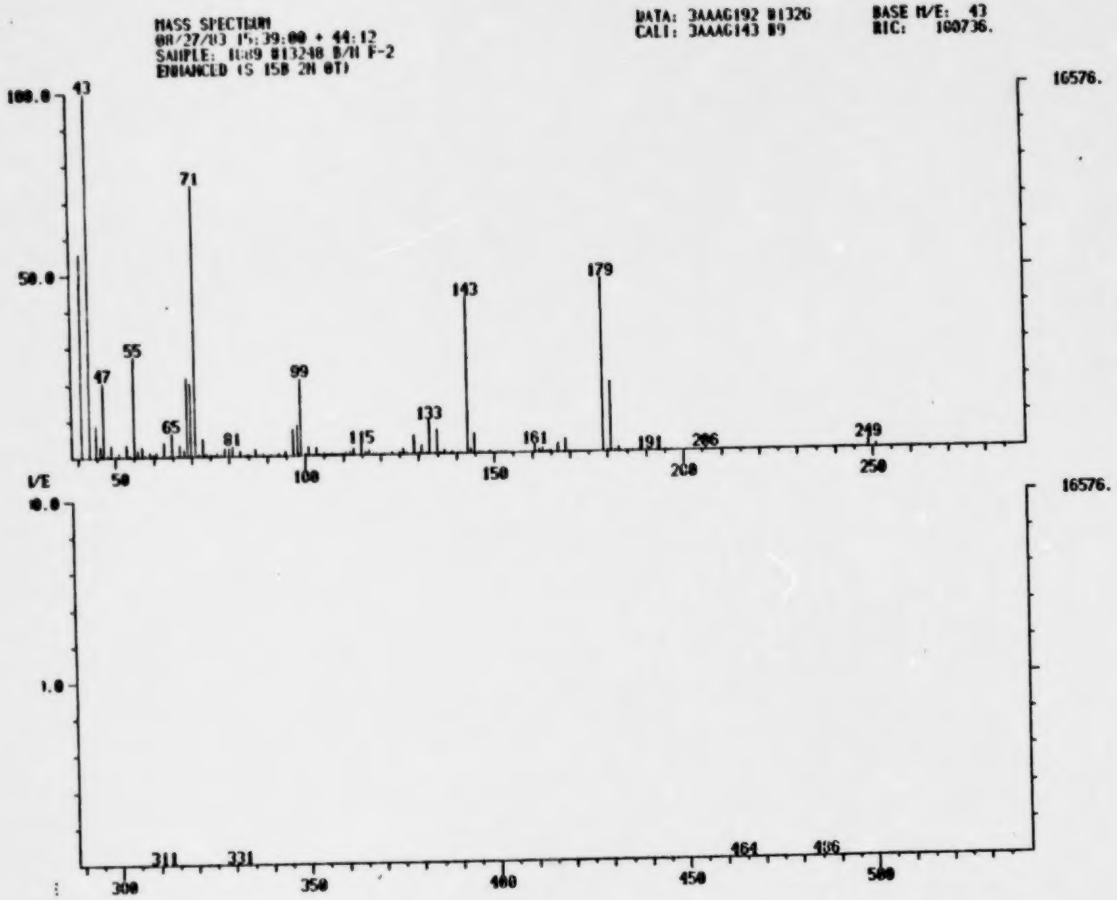


Figure 5.133. Mass spectrum of compound of interest, extract 13248 (base/neutral, fraction 2, scan #1326.

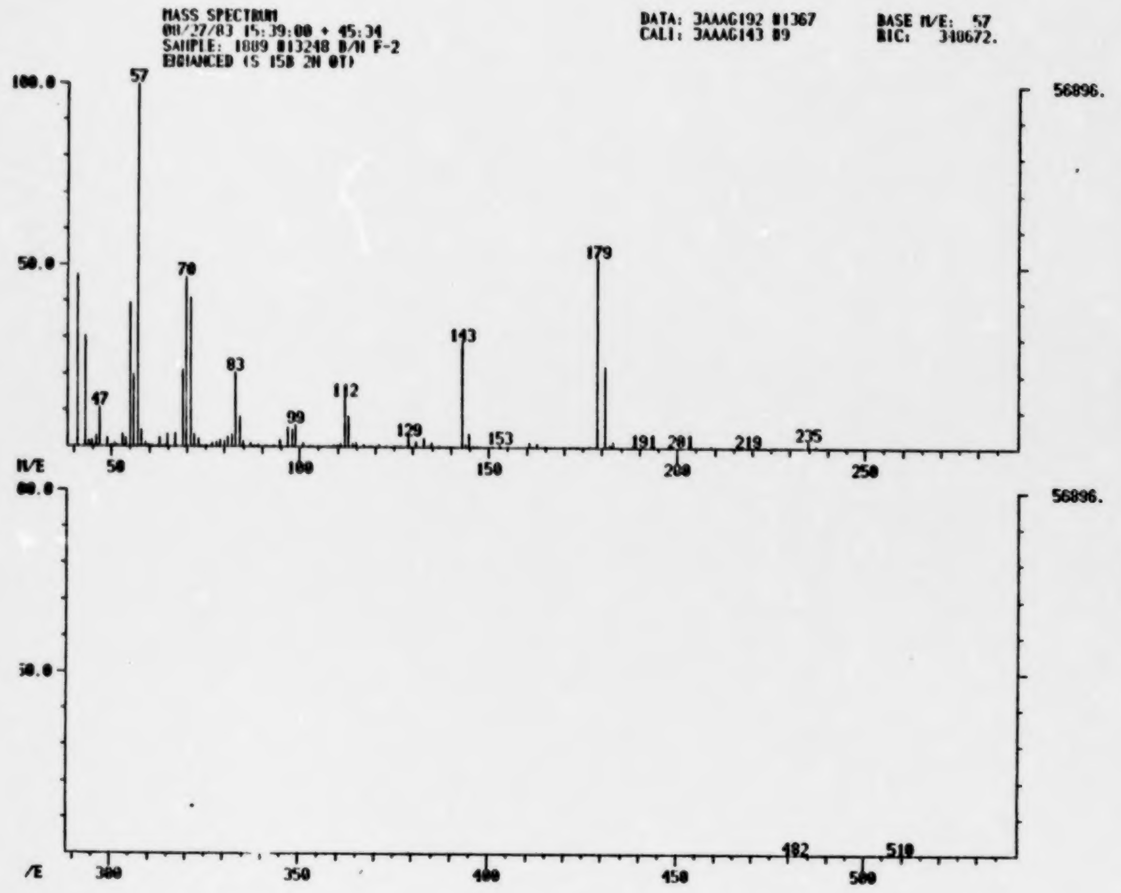


Figure 5.134. Mass spectrum of compound of interest, extract 13248 (base/neutral)), fraction 2, scan #1367.

which indicate that the molecular weight may be 290 (or 292), 304 (or 306), and 346 (or 348), depending on the nature of the species ($(M+1)^+$ or $(M-1)^+$) observed under chemical ionization conditions (Figures 5.135-5.138). Negative mode detection added no additional information.

Extract 19436 (Acid), Plastics and Synthetics Industry, 16 hr Composite

The packed column chromatogram of extract 19436 (acid) is shown in Figure 5.139. The mass spectrum of the compound of interest is presented in Figure 5.140. The capillary chromatogram is shown in Figure 5.141, and the mass spectrum of the compound of interest is presented in Figure 5.142. Accurate mass measurement yields $C_9H_{20}O_3$ as the only possibility. In an effort to isolate the component of interest as the major constituent in a fraction, the extract was subjected to laboratory cleanup, but the compound of interest could no longer be observed after the extract was fractionated. The composition is known from the accurate mass measurement, but the mass spectrum offers very few structural clues. A functional group analysis would be of great benefit in determining a structure for this compound.

Extract 21258 (Base/Neutral), Aluminum Industry, Filter Sludge

The packed column chromatogram of extract 21258 (base/neutral) is shown in Figure 5.143. The mass spectrum of the compound of interest is presented in Figure 5.144. The capillary chromatogram of extract 21258 (base/neutral) is shown in Figure 5.145. The mass spectra corresponding to the compound of interest, as observed from the capillary chromatogram, are presented in Figures 5.146 and 5.147. Accurate mass measurement reduces the possibilities to three for the molecular ion, mass 240: $C_{16}H_{16}O_2$ (error, -2.0 mmu), $C_{15}H_{16}ON_2$ (error, 9.3 mmu), $C_{11}H_{16}O_4N_2$ (error, -6.0 mmu). The extract was subjected to laboratory cleanup procedures in order to be able to utilize other analytical techniques; chromatograms of the three resulting fractions are shown in Figures 5.148-5.150. The compound of interest (Figure 5.151) is observed in the second fraction, but as a minor constituent, so further analytical techniques will not be applicable because of sample size constraints. An additional similar spectrum is obtained in fraction 3. Characterization of the fractions by identification of a few representative constituents was done; compounds identified are tabulated in Table 5.10.

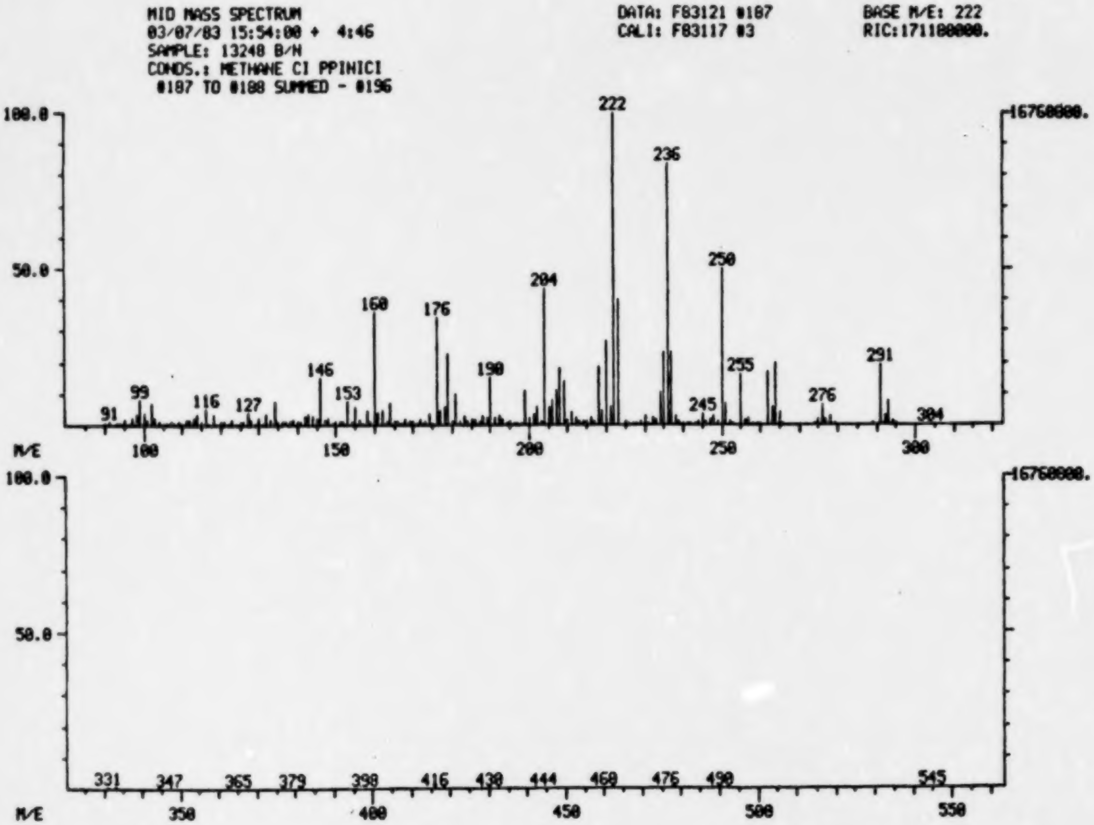


Figure 5.135. Methane chemical ionization mass spectrum of compound of interest, scan #187.

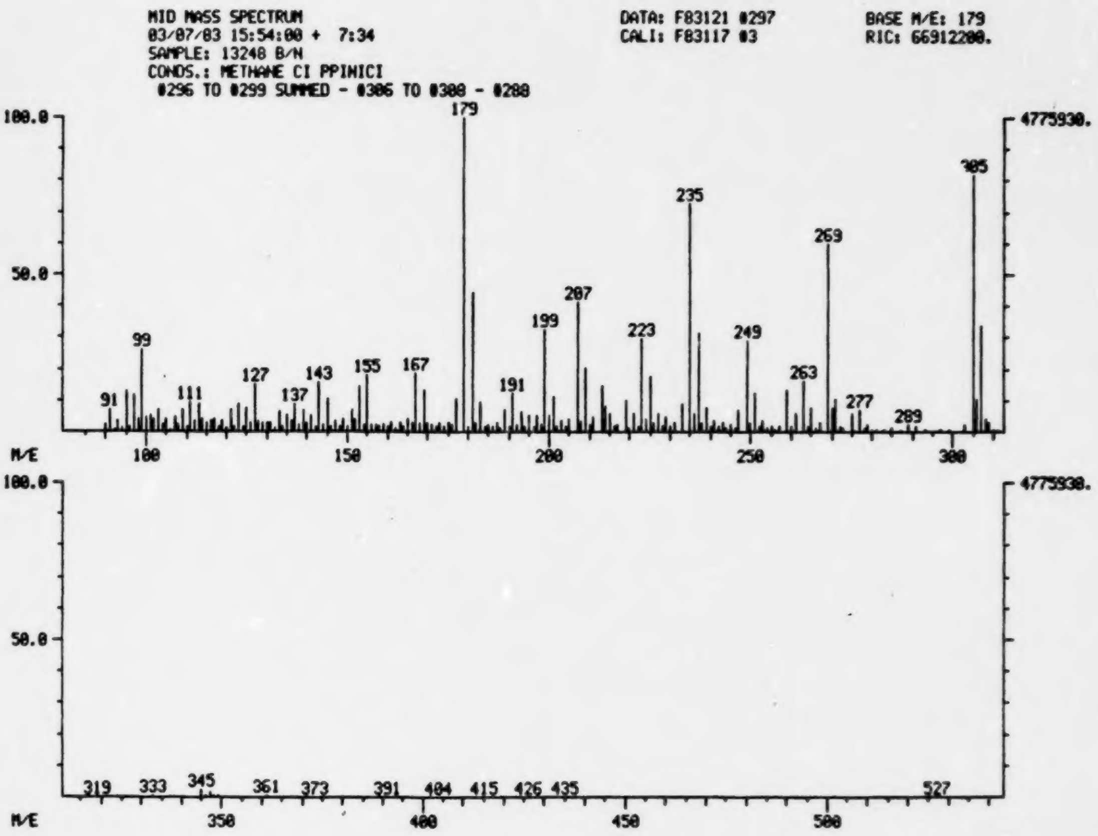


Figure 5.136. Methane chemical ionization mass spectrum of compound of interest, scan #297.

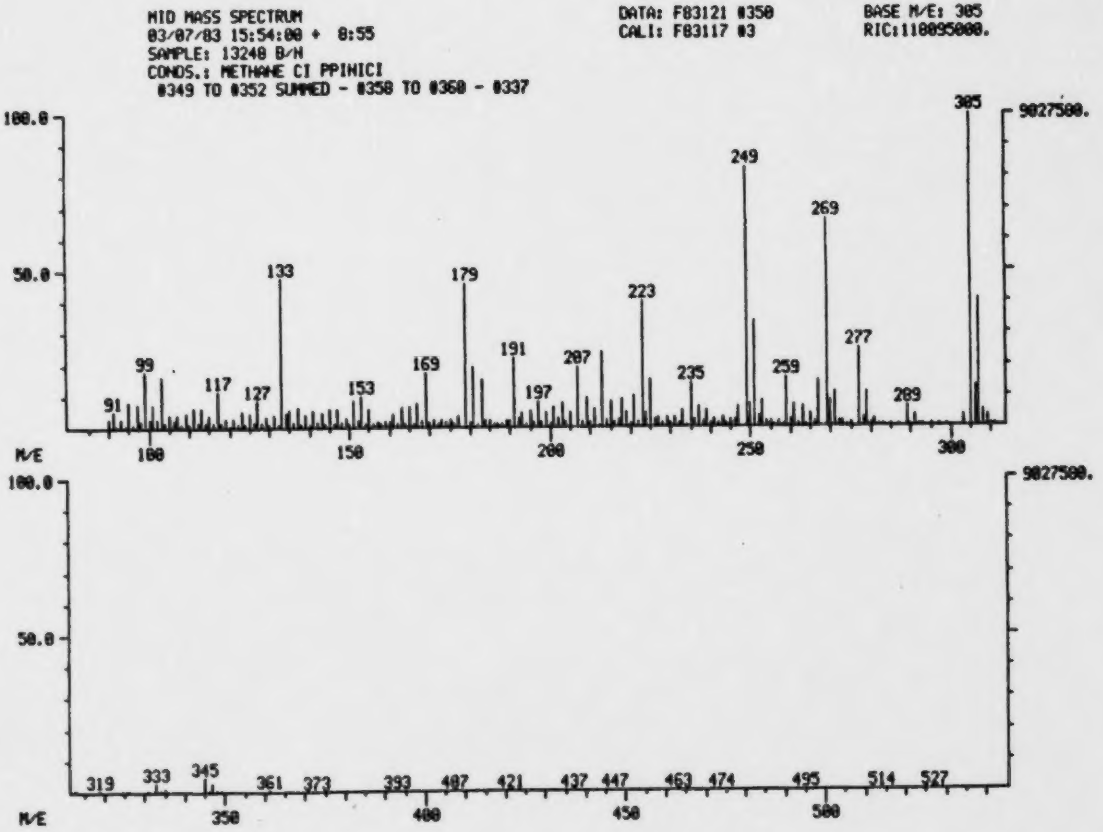


Figure 5.137. Methane chemical ionization mass spectrum of compound of interest, scan #350.

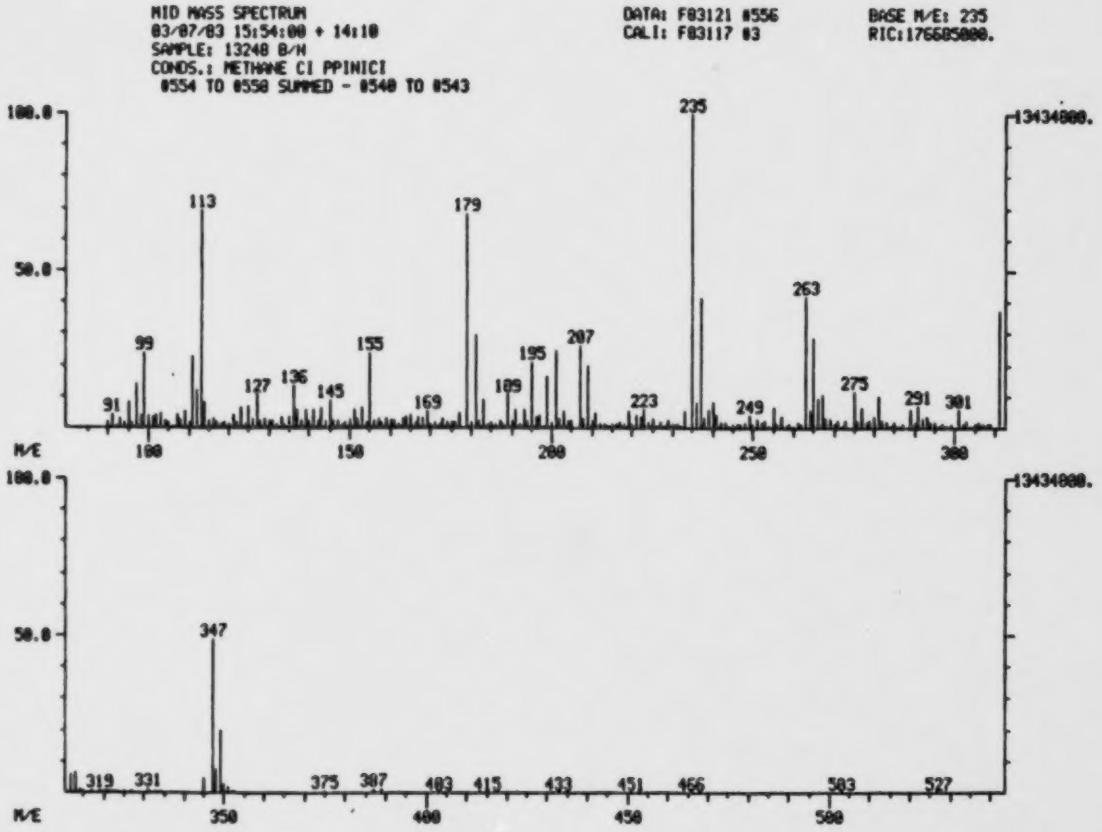


Figure 5.138. Methane chemical ionization mass spectrum of compound of interest, scan #556.

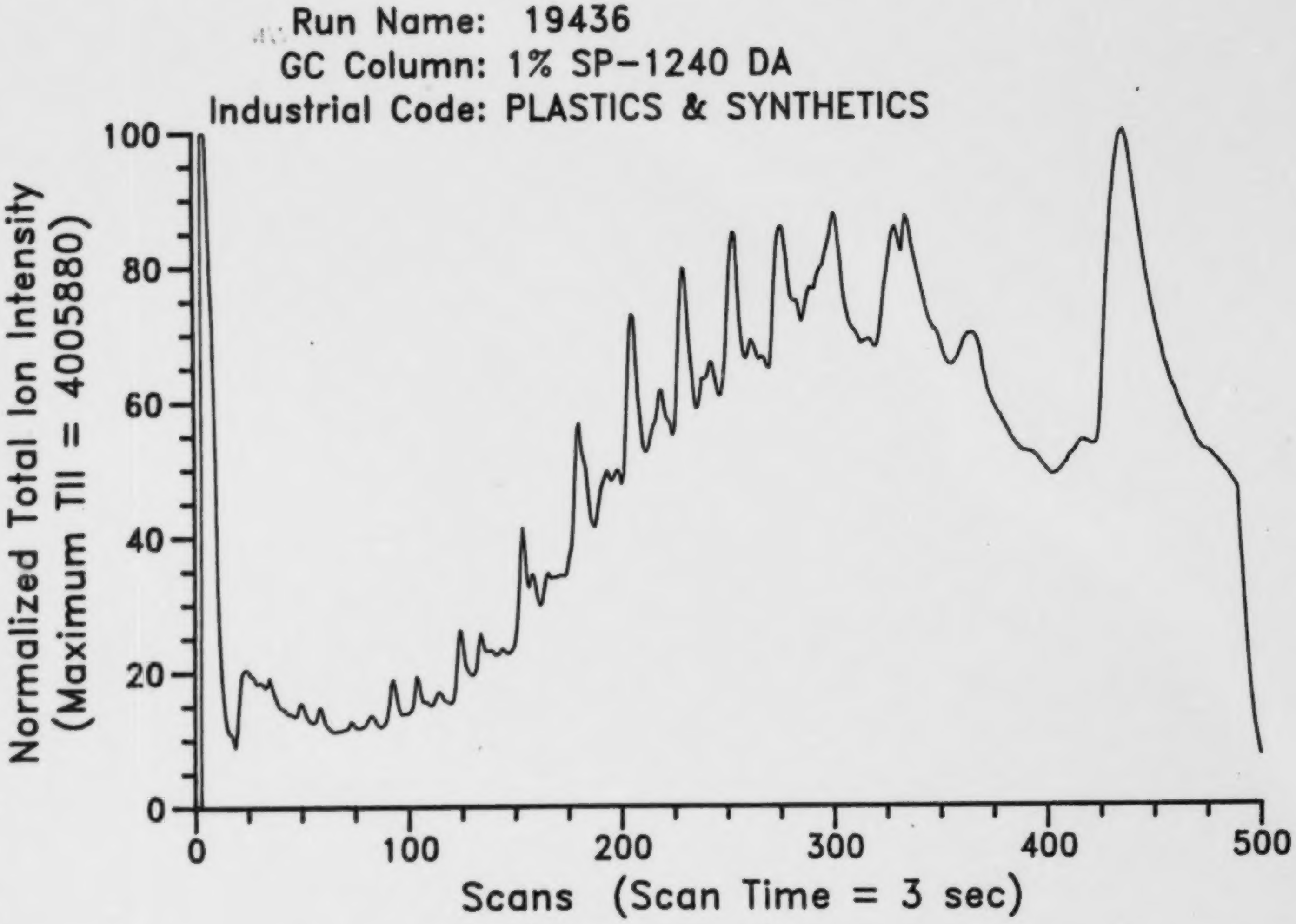


Figure 5.139. Packed column chromatogram, extract 19436 (acid), plastics and synthetics industry.

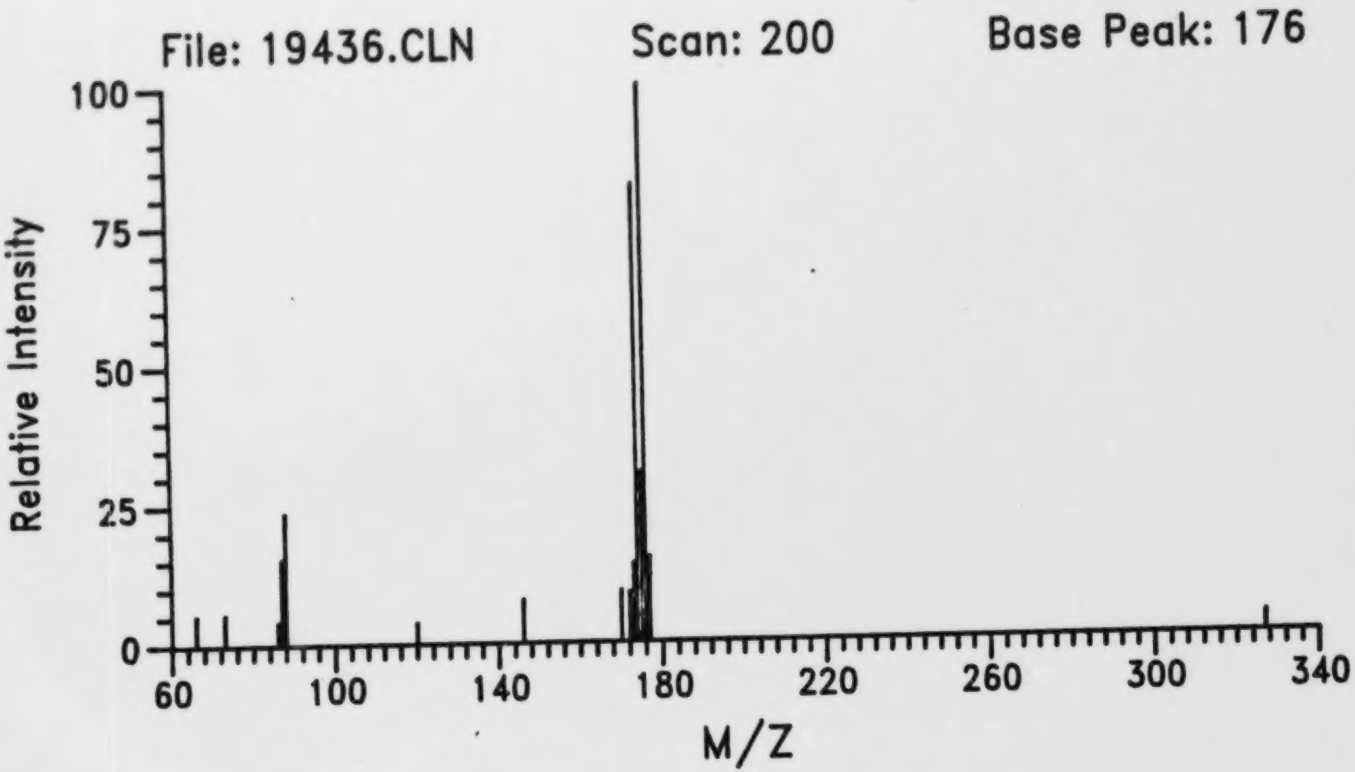


Figure 5.140. Extract 19436 (acid), plastics and synthetics industry. Frequency of occurrence: 9.

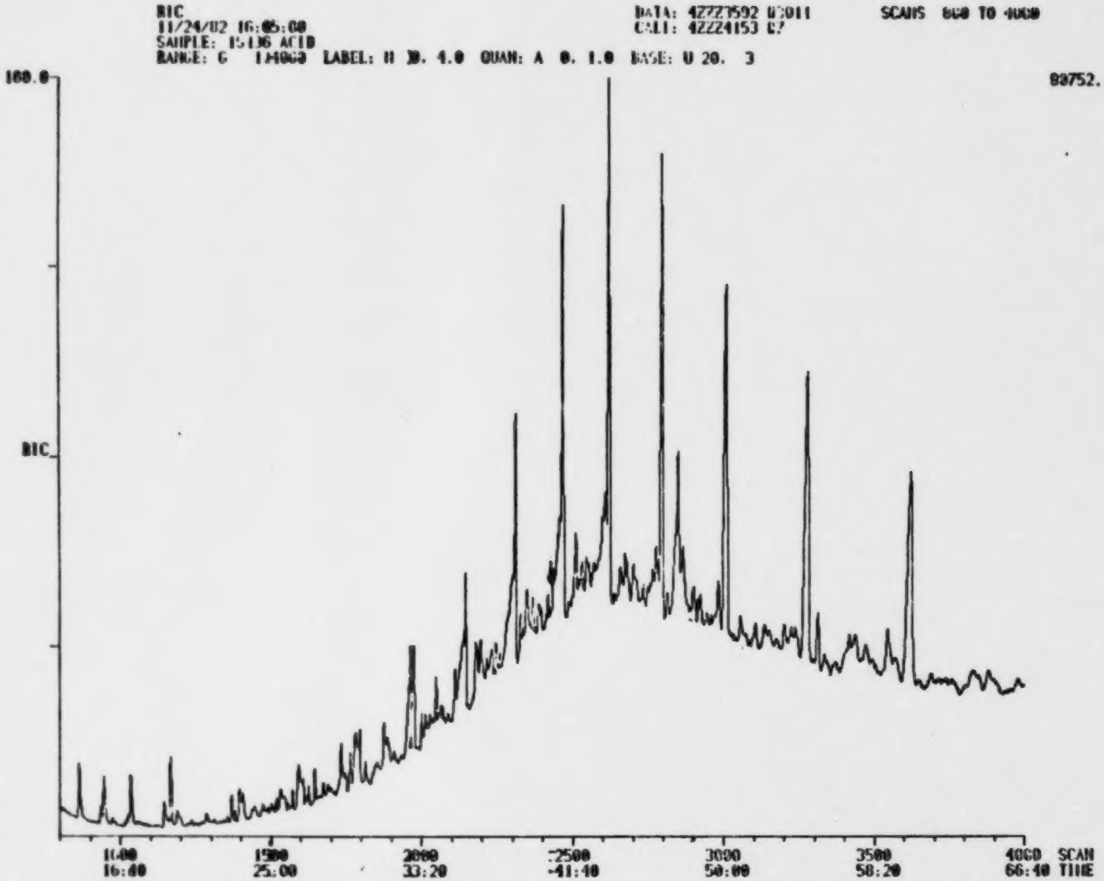


Figure 5.141. Capillary chromatogram of extract 19436 (acid), plastics and synthetics industry.

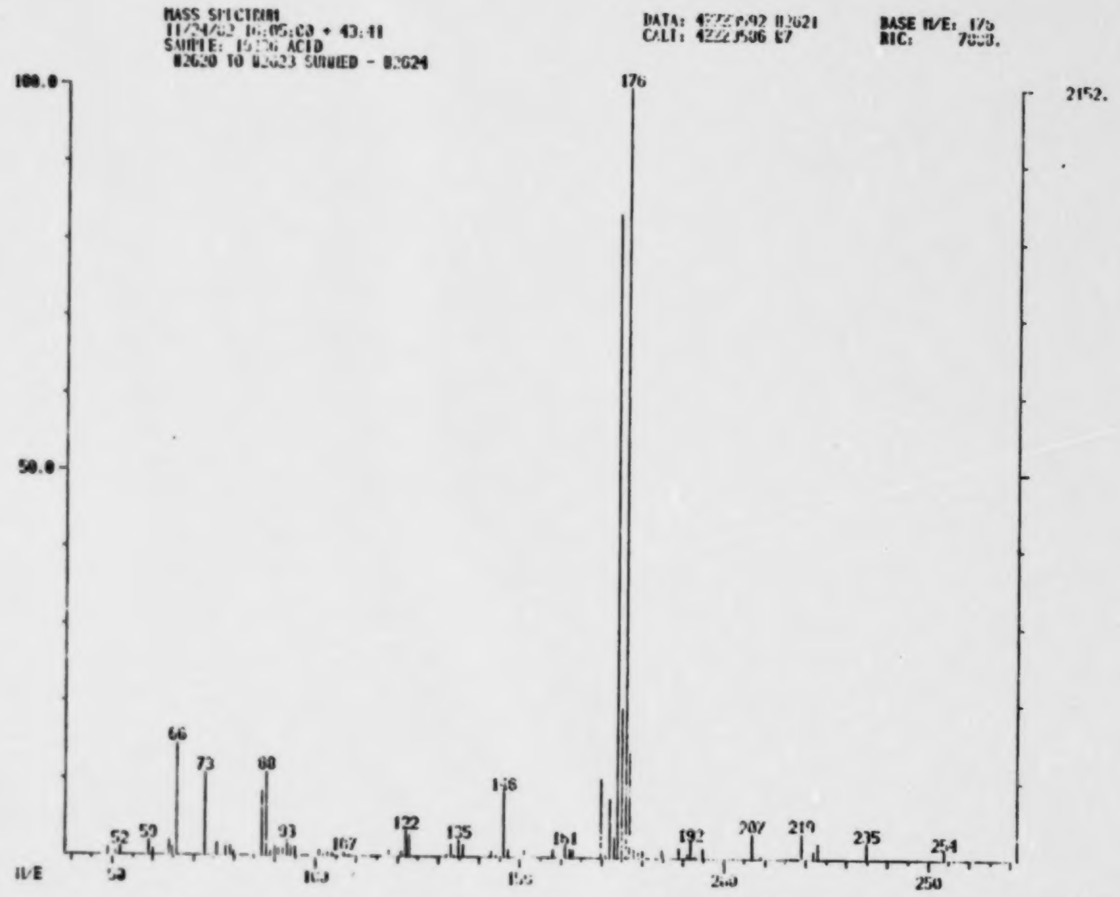


Figure 5.142. Mass spectrum of EPA compound of interest, extract 19436 (acid), plastics and synthetics industry, scan #2621.

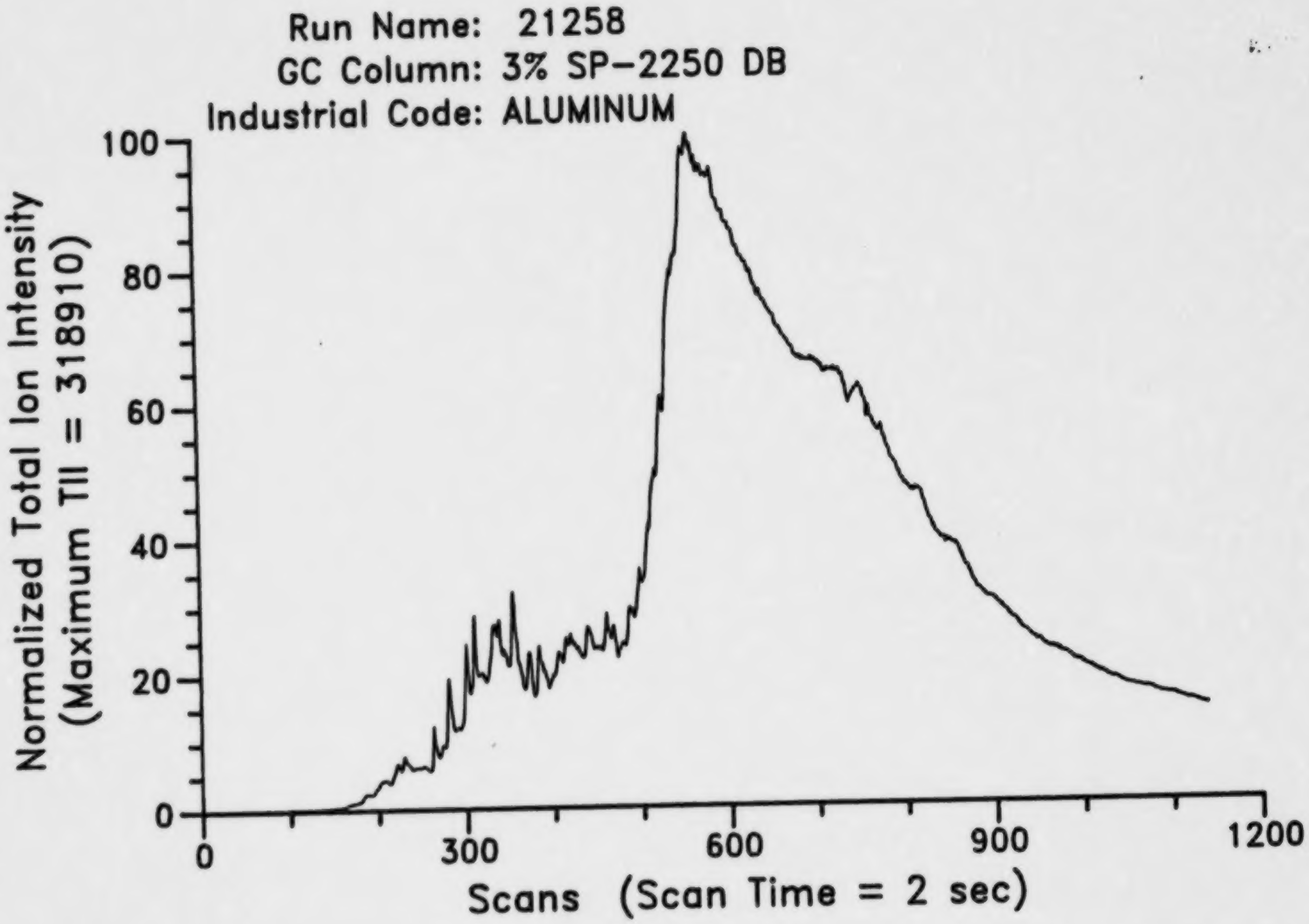


Figure 5.143. Packed column chromatogram, extract 21258 (base/neutral), aluminum industry.

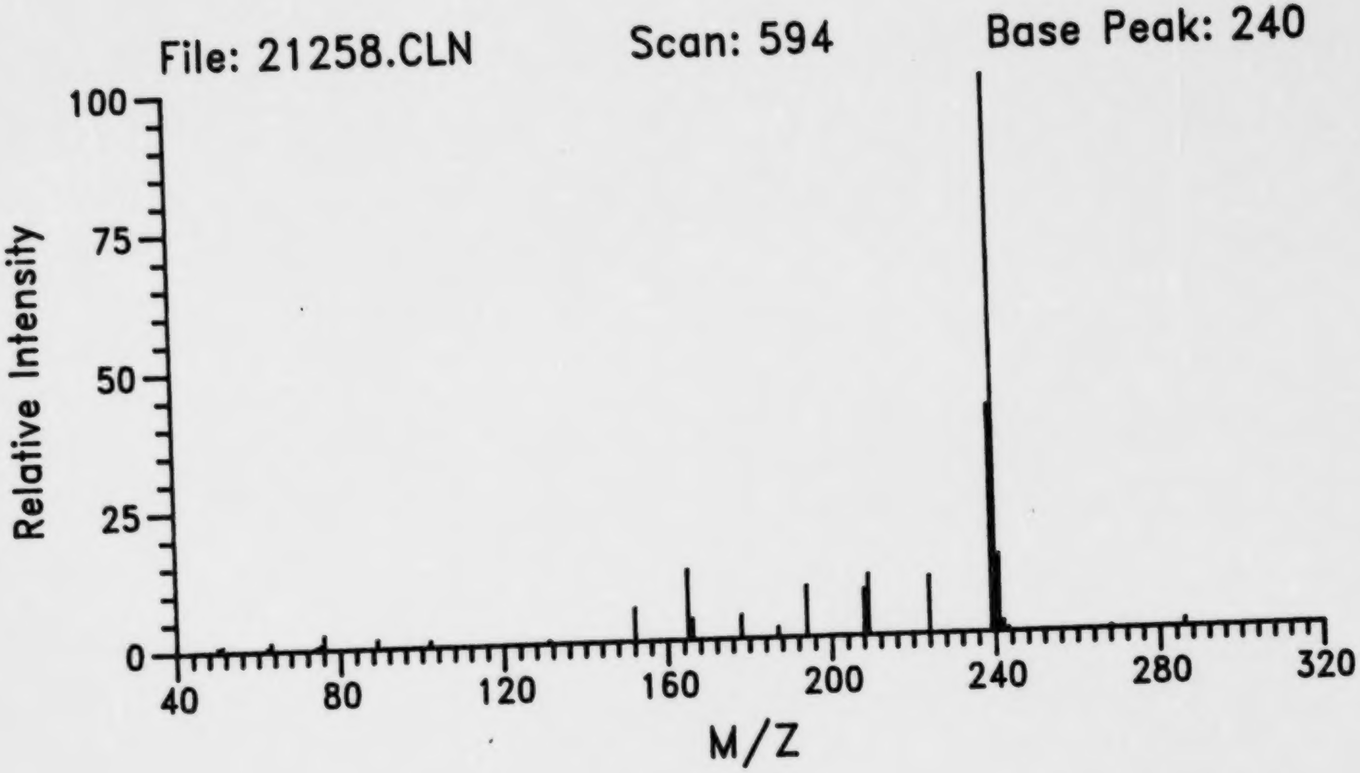


Figure 5.144. Extract 21258 (base/neutral), aluminum industry. Frequency of occurrence: 5.

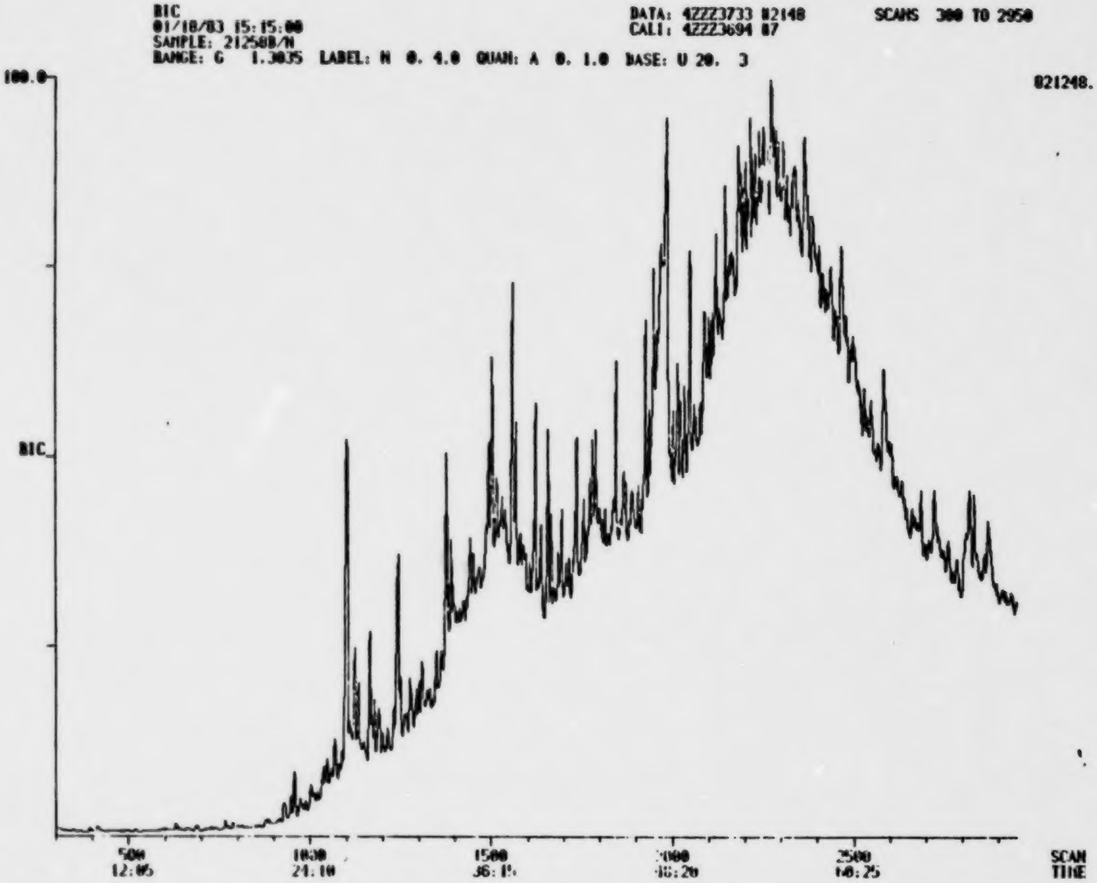


Figure 5.145. Capillary chromatogram of extract 21258 (base/neutral), aluminum industry.

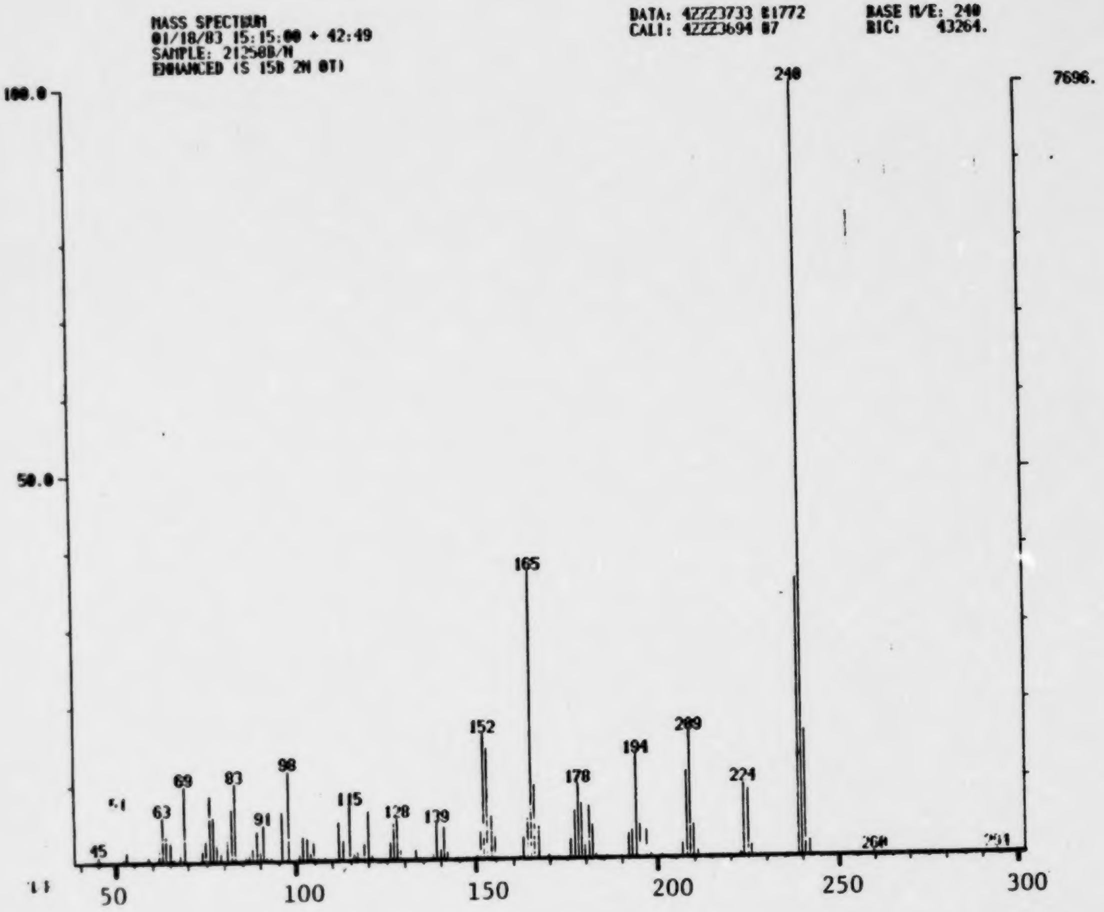


Figure 5.146. Mass spectrum of EPA compound of interest, extract 21258 (base/neutral), aluminum industry, scan #1772.

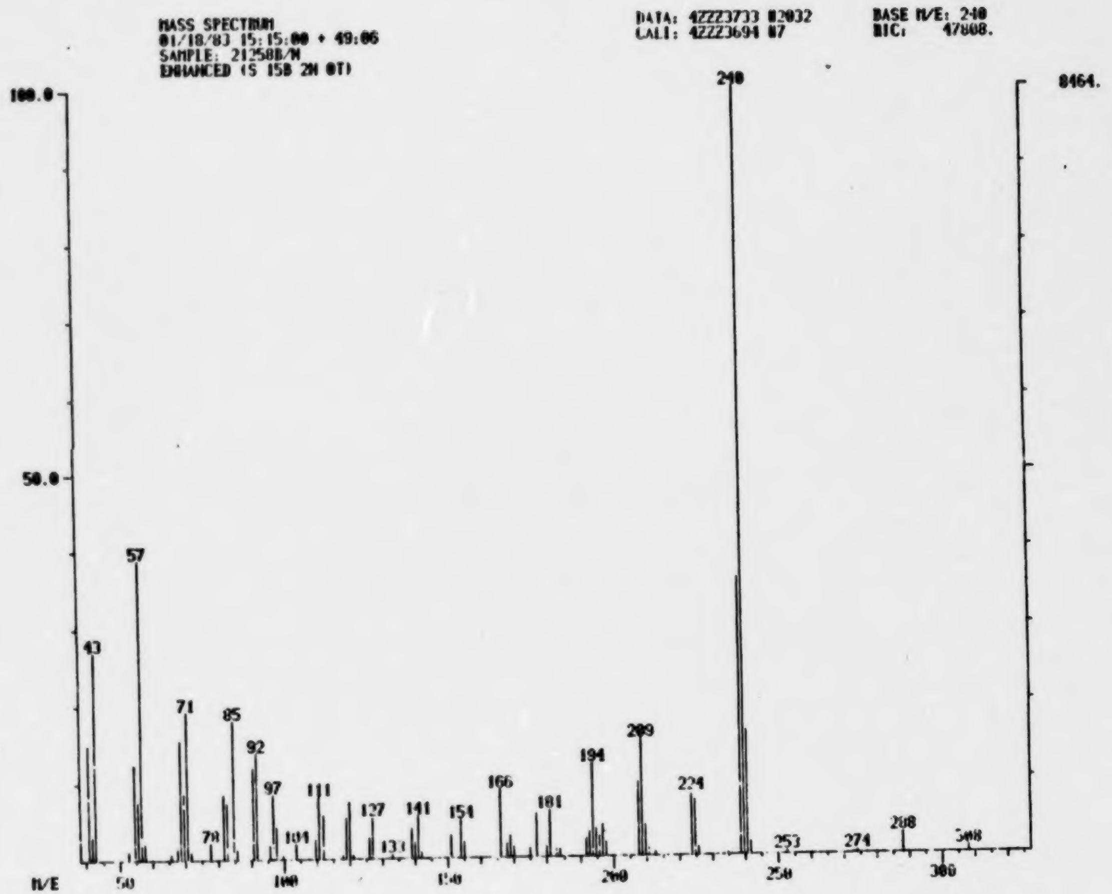


Figure 5.147. Mass spectrum of EPA compound of interest, extract 21258 (base/neutral), aluminum industry, scan #2032.

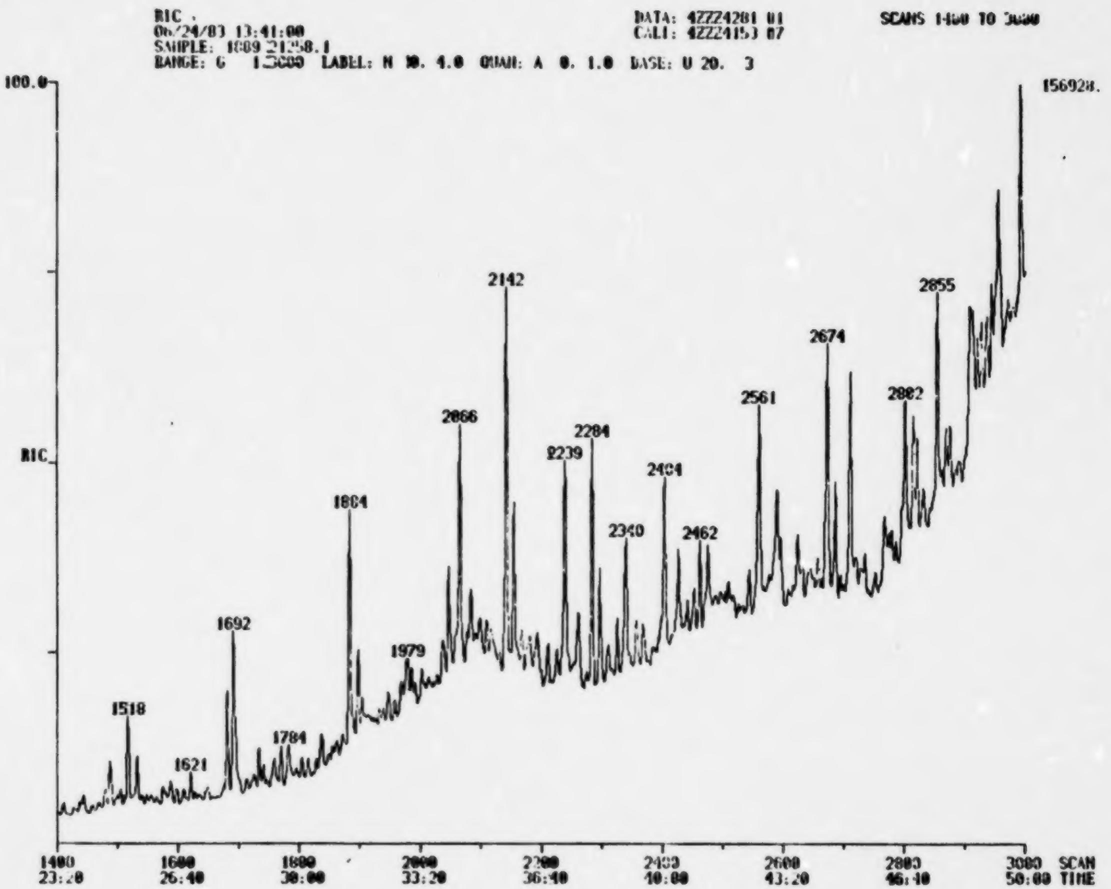


Figure 5.148. Capillary chromatogram of extract 21258 (base/neutral), fraction 1.

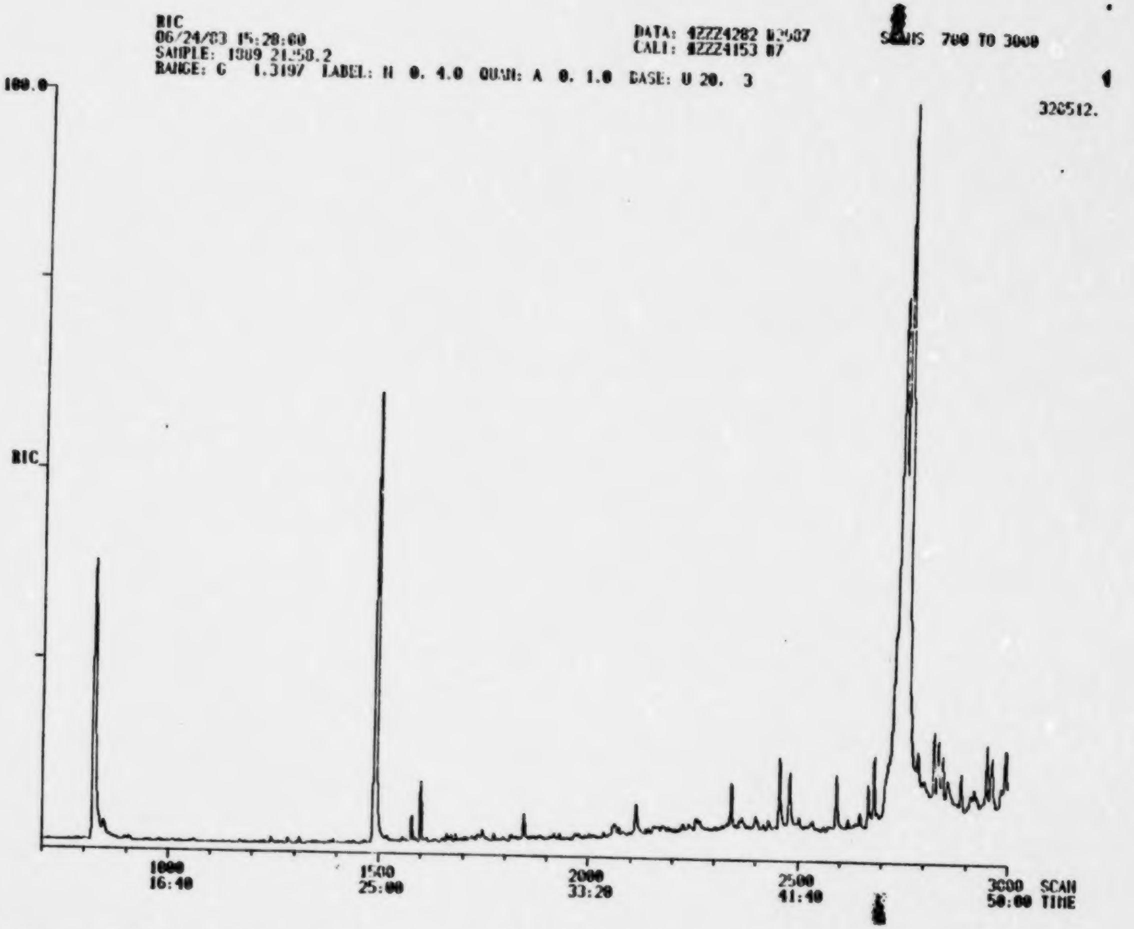


Figure 5.149. Capillary chromatogram of extract 21258 (base/neutral), fraction 2.

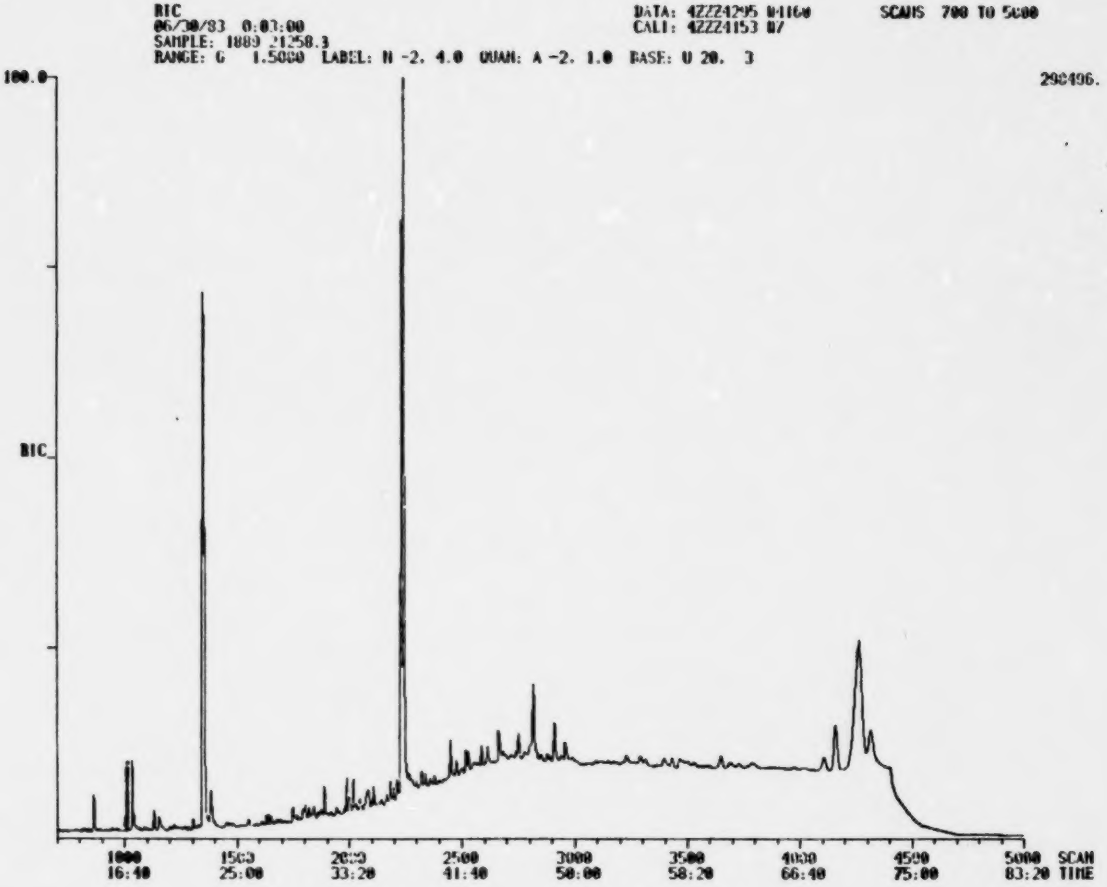


Figure 5.150. Capillary chromatogram of extract 21258 (base/neutral), fraction 3.

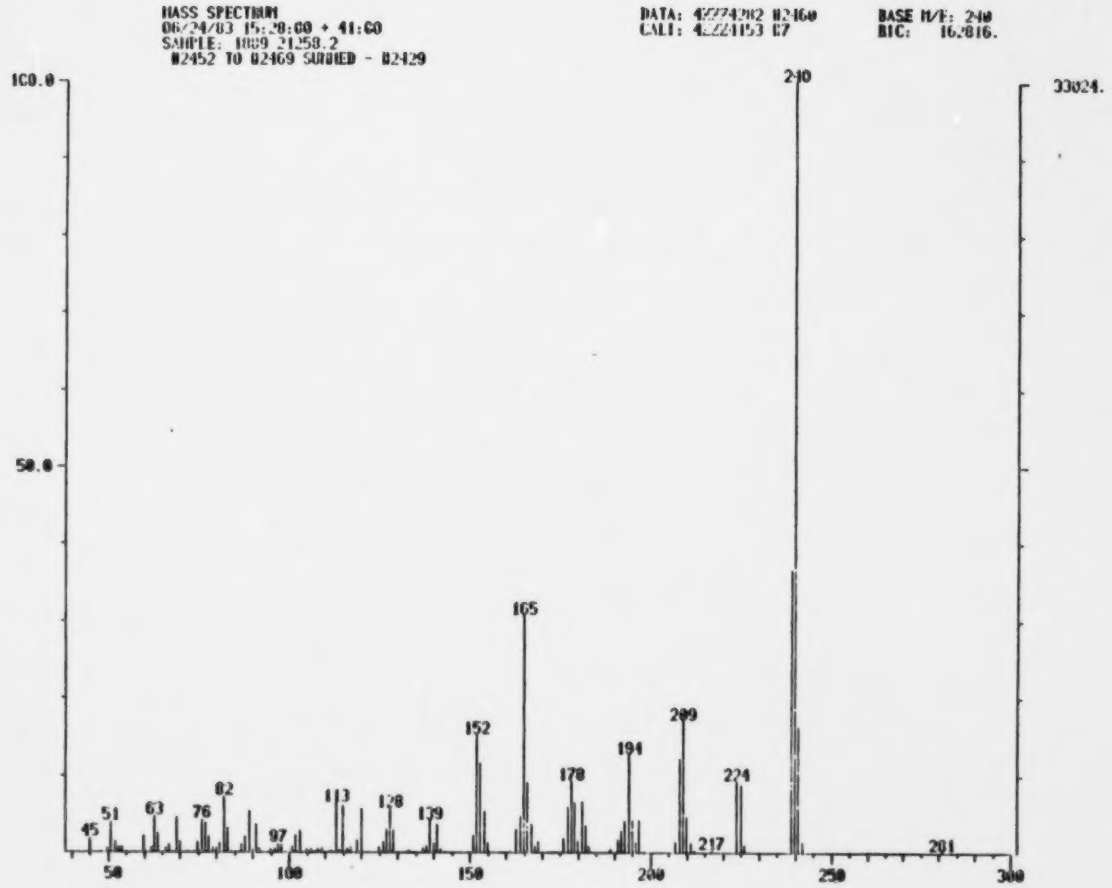


Figure 5.151. Mass spectrum of EPA compound of interest, extract 21258 (base/neutral), fraction 2, scan #2460.

Table 5.10. Components of the fractions of extract 21258 (base/neutral).

Compound	Scan	Fit
Fraction 1		
$C_{14}H_{26}$	1282	-
4-ethyl-2-methylhexane	1518	928
2-butyl-1-octanol	1682	888
pentadecane	1692	994
hexadecane	1884	993
heptadecane	2066	995
3-bromoheptane	2142	967
octadecane	2239	994
2-methyl-1-propene tetramer	2284	750
eicosane	2404	979
heneicosane	2711	994
Fraction 2		
2,3,4,4A,5,6,7,8-octahydro-1,1,4A,7-tetramethyl-1H-benzocyclohepten-7-ol	1494	799
2,6-bis(1,1-dimethylethyl)-2,5-cyclohexadiene-1,4-dione	1579	1000
2,6-bis(1,1-dimethylethyl)-4-ethylphenol	2114	933
hexadecanoic acid	2480	971
9,12-octadecadienoic acid	2744	998
2,3-dihydroxypropyl-9-octadecenoate	2758	936
2-hydroxyethyl 9-octadecenoate	3108	983
Fraction 3		
4-hydroxy-4-methyl-2-pentanone acetic acid	866	975
3-(2,2,6-trimethyl-7-oxabicyclo[4.1.0]hept-1-yl)-2-propenal	1037	985
pyrene	4264	985

Conclusions

From a study of the results of fractionation of the extracts, it is clear that one goal is realized: the fractionation process does, indeed, simplify the extract. In all cases where fractionation was used with an extremely complex chromatogram, at least the most polar fraction (fraction 3) could be characterized in a straightforward manner. Most of these polar constituents of the extract could have been observed only with difficulty in the original extract. As a thorough fractionation process (*i.e.*, quantitative separation of types of constituents), this particular fractionation process shows considerable overlap. Polynuclear aromatic compounds tend to be observed in all of the fractions. Alkane and alkene hydrocarbons overlap both fractions 1 and 2. Fraction 1, which contains the hydrocarbons, tends to be as complex as the original unfractionated extract. Complexity in this fraction usually presents no problem, however, since the objective of the fractionation is usually to observe constituents of the extract buried under the hydrocarbon background. Loss of the component of interest appears to be a very real hazard, as it occurred in approximately 25% of the extracts fractionated. A final elution with methanol as fraction 4 should yield all the rest of the polar compounds, if any are still retained. It would be an advantage to devote a considerable length of time to method development, in order to effect a more complete and quantitative fractionation.

ANALYSES OF EXTRACTS INCORPORATING UNACON/CAPILLARY GC/FT-IR ANALYSES

With an awareness of stringent requirements for sample size, extracts to be subjected to FT-IR analysis were carefully selected to provide the best opportunity for success. Several factors influenced selection of a particular extract: 1) the peak for the compound of interest was a major peak in the capillary chromatogram; 2) the region of the chromatogram in which the peak for the compound of interest eluted was relatively free of possibly interfering components; 3) accurate mass measurement had been performed so that at least a most probable composition (and even, possibly, a tentative structure) could be postulated; and 4) the information sought from FT-IR was functional group analysis, usually for oxygen-containing moieties. The technique also took advantage of the sample concentrating capabilities of the Unacon Automatic Sample Concentrator, to enhance the concentration of the component of interest as much as possible. These analyses are summarized in Table 5.11.

Extract 5118 (Acid), Amusements and Athletic Goods Industry, Paint Strip

The packed column chromatogram for extract 5118 (acid) is presented in Figure 5.152. The mass spectrum of the EPA compound of interest is shown in Figure 5.153. From an inspection of the spectrum in Figure 5.153, a tentative identification of the compound of interest as a tetrachlorophenol isomer can readily be made. The capillary chromatogram of extract 5118 (acid) is shown in Figure 5.154. The compound of interest is indeed observed, as evident from the mass spectrum from the capillary assay shown in Figure 5.155. Rather than purchasing standards for the three possible isomers and confirming the identification by co-injection, the extract was subjected to capillary GC/FT-IR analysis in order to identify the particular isomer. The GC/FT-IR analysis was unsuccessful, however. All of the ramaining sample was expended but no tetrachlorophenol was observed.

Extract 5855 (Acid), Pesticides Manufacturing Industry, Sanitary Composite

The packed column chromatogram for extract 5855 (acid) is presented in Figure 5.156. The mass spectrum of the EPA compound of interest is shown in Figure 5.157. The capillary chromatogram of extract 5855 (acid) is presented in Figure 5.158. The mass spectrum of the compound of interest as observed in the capillary assay is shown in Figure 5.159. This same spectrum was observed in a survey of industrial wastewater by Battelle as reported under EPA Contract No. 68-01-4350. The spectrum matched poorly with mass spectra of butyl phenol and phthalates. GC/FT-IR showed the compound to be a phenol with an alkoxy group present. No further work was done and no full structure elucidation could be done. Accurate mass measurement data for three of the major peaks of the mass spectrum are presented in Figure 5.160. Several structural features are evident from a careful study of the mass spectral data. The molecule exhibits a loss of 15 mass units, so a methyl group is present. The ion of mass 77 suggests the presence of a benzene ring, and the presence of an ion of mass 91 says that at least one carbon atom is attached to this

Table 5.11. Extract Analysis Incorporating GC/FT-IR

Extract	Industry	Analytical Techniques Used	Result
5118 (acid)	Amusements and athletic goods	Capillary GC/MS analysis	Compound of interest observed; tentatively identified.
		Unacon/capillary GC/FT-IR	Compound of interest not observed.
5855 (acid)	Pesticides manufacturing	Capillary GC/MS analysis	Compound of interest observed; some structural features elucidated.
		Accurate mass measurement	Possibilities narrowed to one.
		Unacon/capillary GC/FT-IR	Functional groups identified; structure suggested.
		Custom synthesis	Rejected as too expensive.
11338 (acid)	Organics and plastics	Capillary GC/MS analysis	Compound of interest found; contains F and O.
		Accurate mass measurement	Two probable compositions.
		Unacon/capillary GC/FT-IR	Compound of interest not observed.
11536 (base/neutral)	Inorganic chemicals	Capillary GC/MS analysis	Compound of interest found.
		Accurate mass measurement	Three/four possibilities.
		Chemical ionization mass spectrometry (methane, isobutane)	No conclusive data.
		Unacon/capillary GC/FT-IR	Compound of interest not observed.
11977 (base/neutral)	Electronics	Capillary GC/MS analysis	Compound of interest found.
		Accurate mass measurement	One possibility; tentative identification.
		Unacon/capillary GC/FT-IR	Compound of interest not observed.
18959 (acid)	Pulp and paper	Capillary GC/MS analysis	Compound of interest found.
		Accurate mass measurement	One possibility.
		Chemical ionization mass spectrometry	Molecular weight probably 176; tentative structure.
		Unacon/capillary GC/FT-IR	Compound of interest not observed.

Table 5.11 (continued)

Extract	Industry	Analytical Techniques Used	Result
20250 (base/ neutral)	Explosives	Capillary GC/MS analysis	Compound of interest found.
		Accurate mass measurement	One possibility.
		Unacon/capillary GC/FT-IR	Compound of interest not observed.

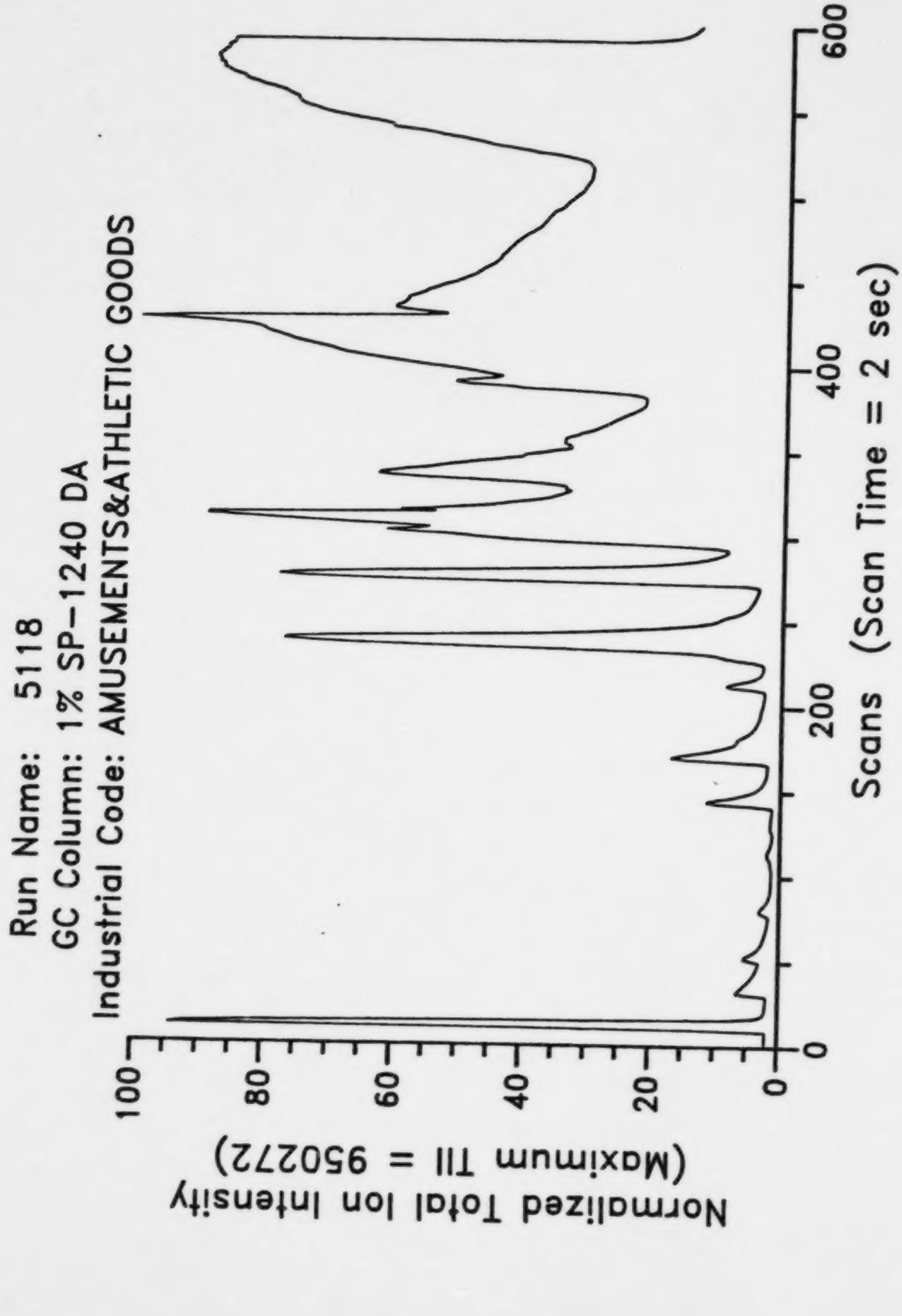


Figure 5.152. Packed column chromatogram of extract 5118 (acid), amusements and athletic goods industry.

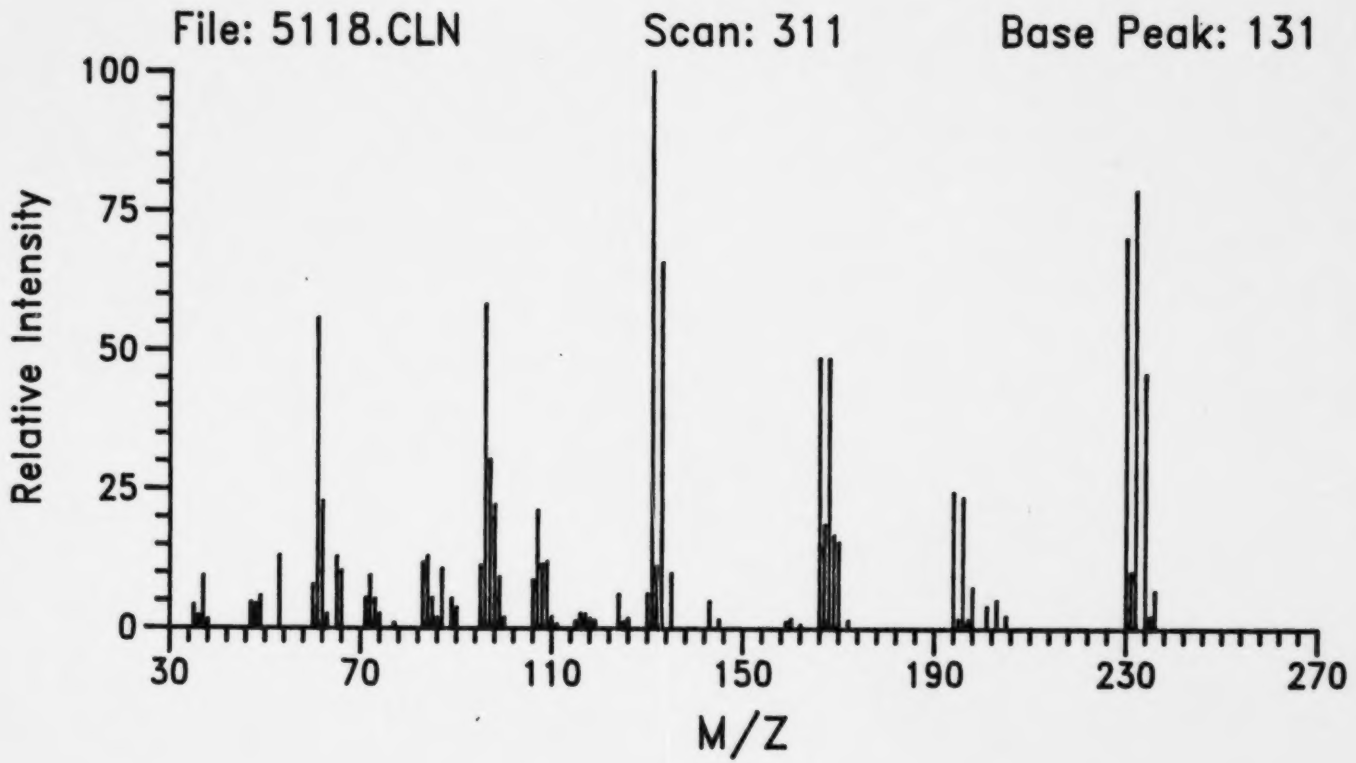


Figure 5.153. Extract 5118 (acid), amusements and athletic goods industry. Frequency of occurrence: 8.

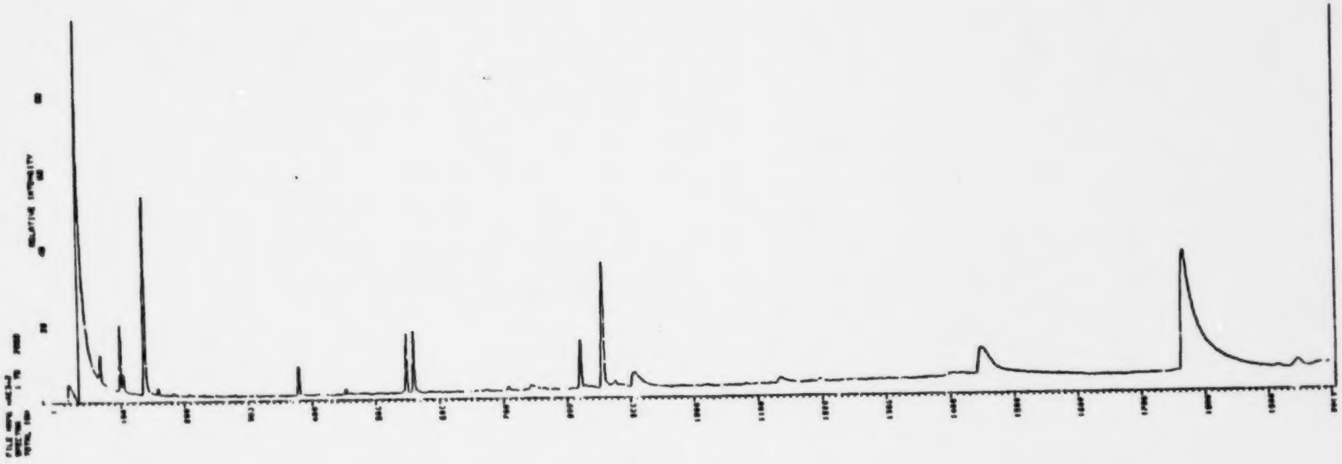


Figure 5.154. Capillary chromatogram of extract 5118 (acid), amusements and athletic goods industry.

2,3,4,6-tetrachlorophenol

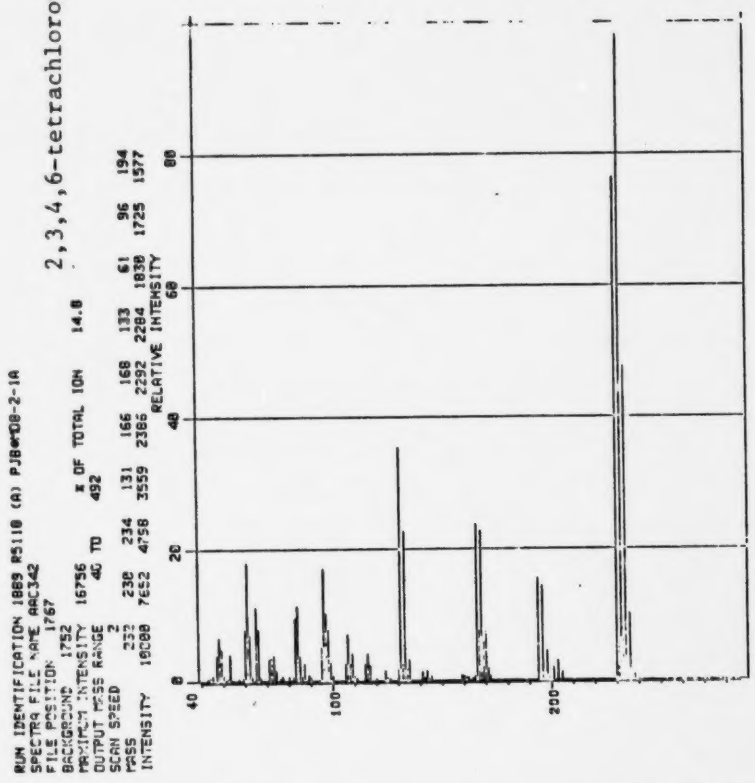


Figure 5.155. Mass spectrum of EPA compound of interest, extract 5118 (acid), amusements and athletic goods industry, scan #1767.

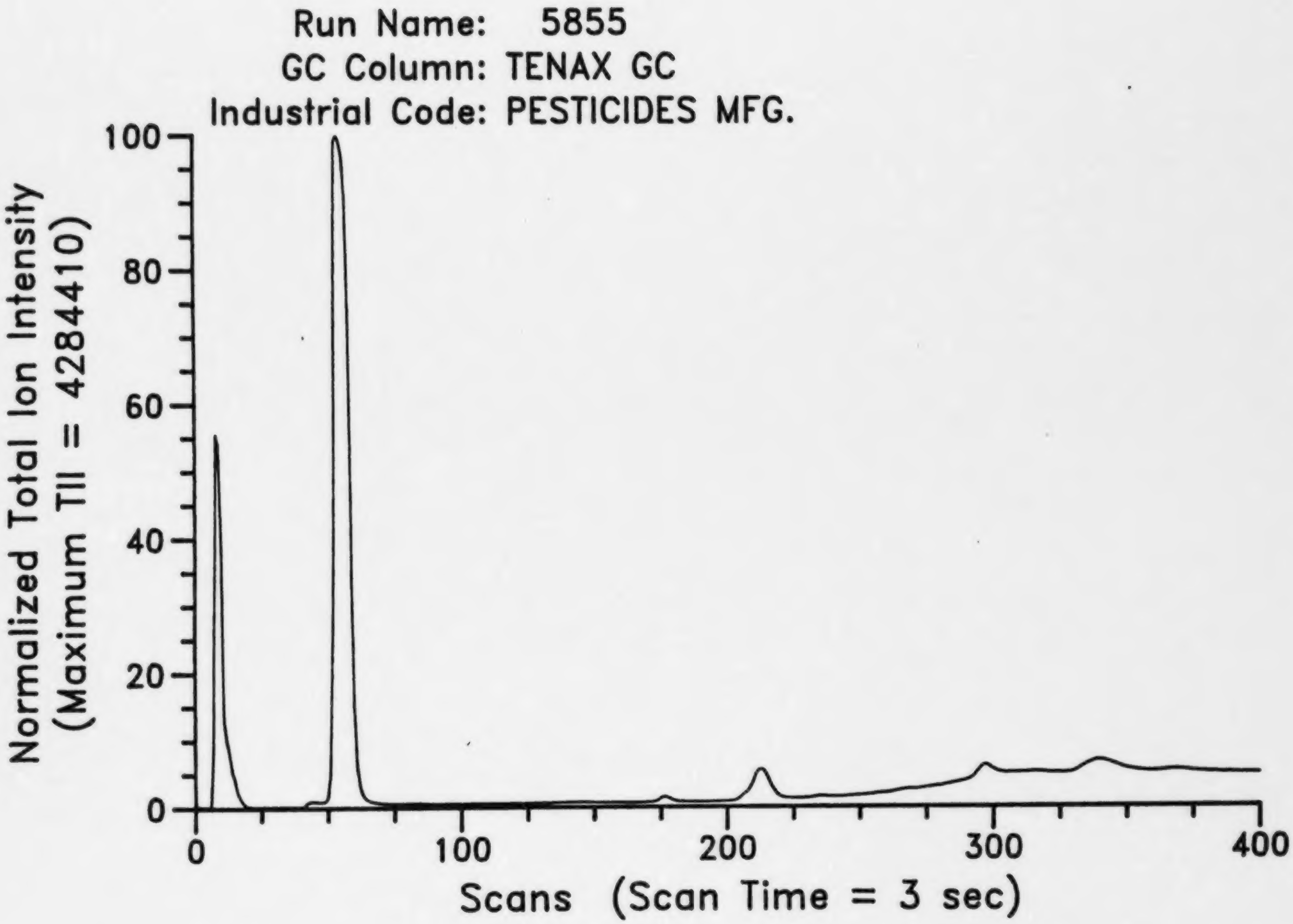


Figure 5.156. Packed column chromatogram, extract 5855 (acid), pesticides manufacturing industry.

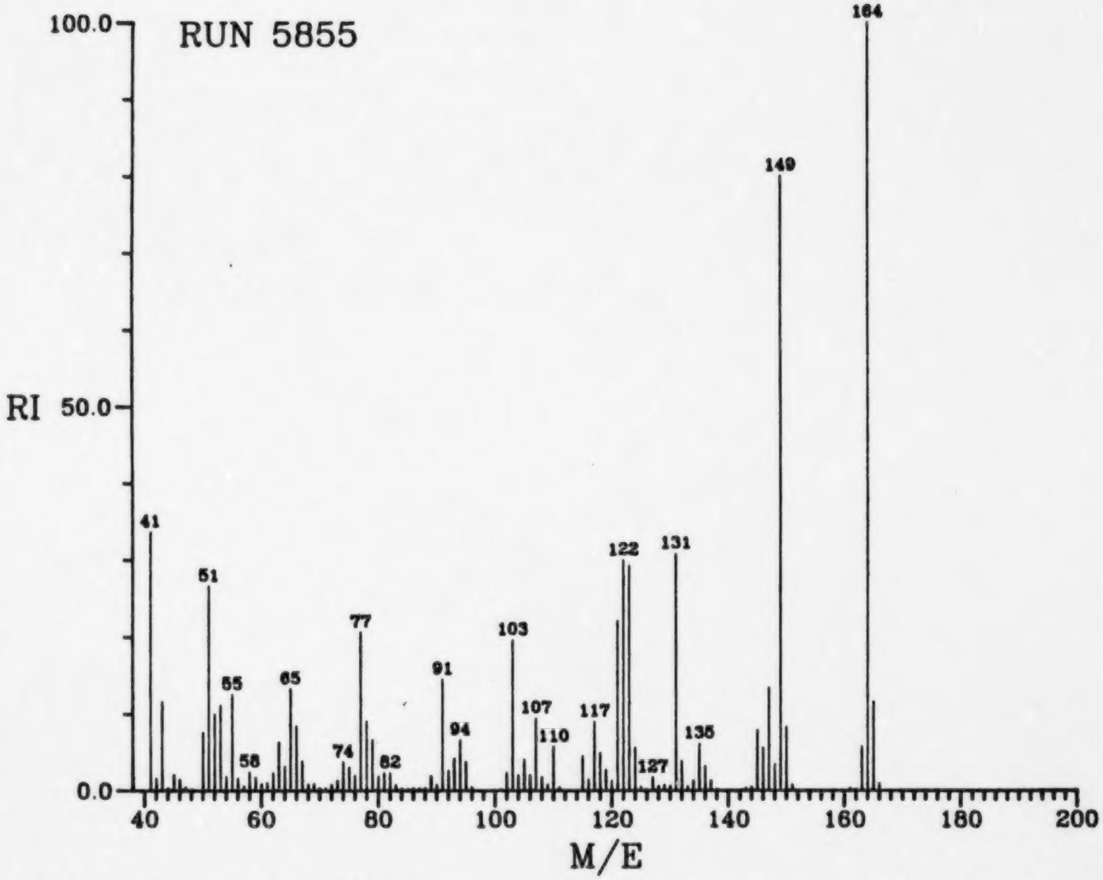


Figure 5.157. Extract 5855 (acid), pesticides manufacturing industry. Frequency of occurrence: 5.

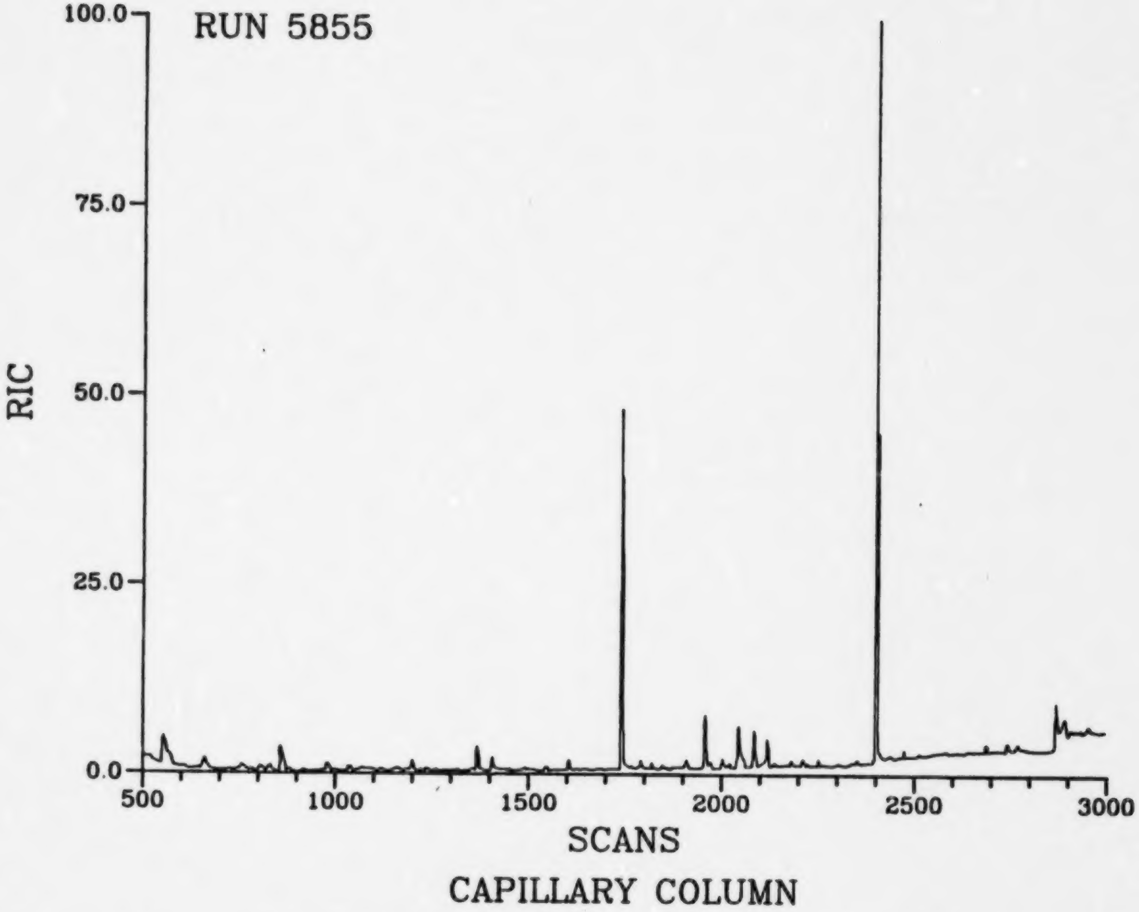


Figure 5.158. Capillary chromatogram of extract 5855 (acid), pesticides manufacturing industry.

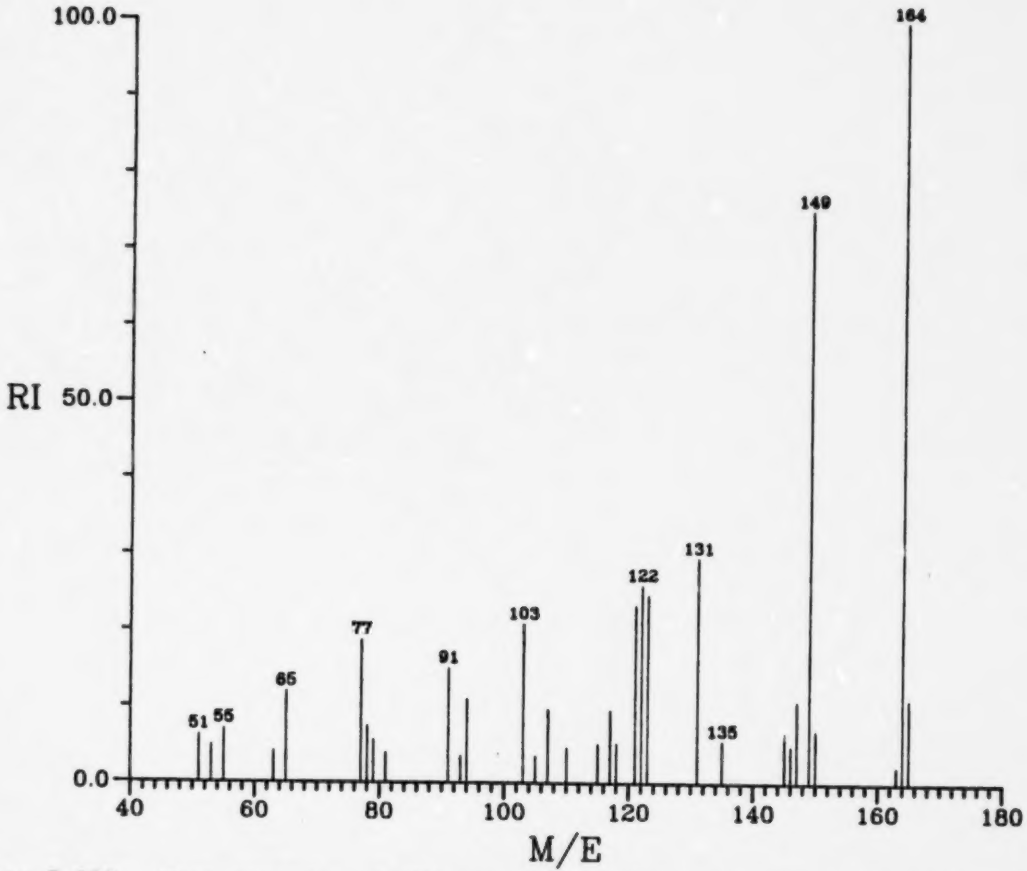


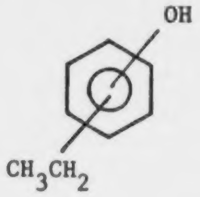
Figure 5.159. Mass spectrum of EPA compound of interest, extract 5855 (acid), pesticide manufacturing industry, scan #2400.

Figure 5.160. Accurate mass measurement data, extract 5855 (acid), pesticides manufacturing industry.

High Resolution Mass Data

M/E	C	H	^{16}O	F	^{32}S	P	MMU	OBS.MASS
164	10	12	2	0	0	0	−4.8	164.0885
	7	13	3	1	0	0	−3.6	
	8	11	0	3	0	0	−7.2	
	7	16	2	0	1	0	−1.4	
	7	17	2	0	0	1	8.1	
	7	17	0	0	1	1	−9.6	
149	9	9	2	0	0	0	3.9	149.0563
	6	10	3	1	0	0	5.1	
	7	8	0	3	0	0	1.5	
	6	13	2	0	1	0	7.3	
	4	12	0	3	1	0	4.9	
	9	10	0	0	0	1	−4.3	
	6	11	1	1	0	1	−3.2	
	6	14	0	0	1	1	−0.9	
	3	15	1	1	1	1	0.2	
131	9	7	1	0	0	0	1.1	131.0486
	6	8	2	1	0	0	2.2	
	4	7	0	4	0	0	−0.2	
	6	11	1	0	1	0	4.5	
	3	12	2	1	1	0	5.6	
	6	9	0	1	0	1	−6.0	
	3	10	1	2	0	1	−4.9	
	3	13	0	1	1	1	−2.6	

benzene ring. The presence of an ion at mass 135 suggests that an ethyl group might be attached to the aromatic ring, since a loss of 29 mass units can occur. The presence of an aromatic ring with at least two carbon atoms attached limits the possibilities from accurate mass measurement to two, $C_{10}H_{12}O_2$ and $C_8H_{11}F_3$. The presence of a small peak in the mass spectrum at mass 94 suggests than an -OH group might also be attached to the aromatic ring. If one oxygen is suspected to be present, then the possibilities from accurate mass measurement are limited to one, $C_{10}H_{12}O_2$. Structural features deduced so far lead to the partial structure below:



with two carbon atoms and one oxygen atom not accounted for. There is no direct indication of the nature of the functional group containing the other oxygen atom. Functional group analysis would be of great benefit in this case, and, since the peak corresponding to the compound of interest in the chromatogram is major and in a relatively interference-free region of the chromatogram, the extract was submitted for analysis by Unacon/capillary gas chromatograph/FT-IR. The spectrum obtained for the unknown is shown in Figure 5.161. The library of the FT-IR spectrophotometer system does not contain a spectrum which is an exact match to the unknown, but two closely corresponding compounds are shown in Figures 5.162 and 5.163. The parent compound is obviously a dihydrobenzofuran, an identification consistent with all mass spectrometric data available.

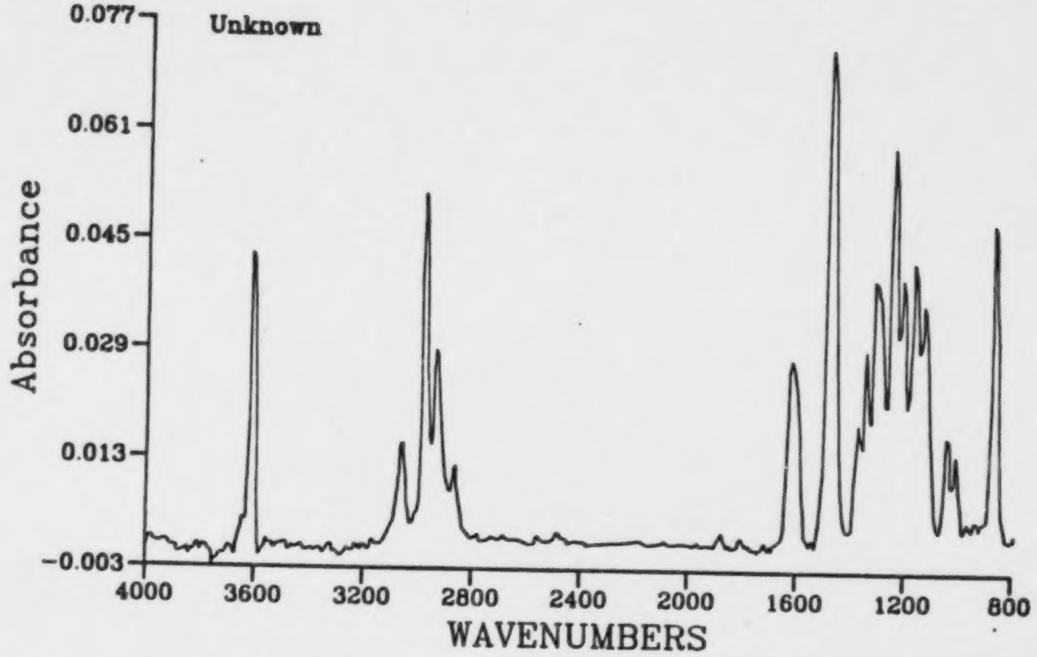


Figure 5.161. Unacon/capillary GC/FT-IR analysis of EPA compound of interest, extract 5855 (acid), pesticides manufacturing industry.

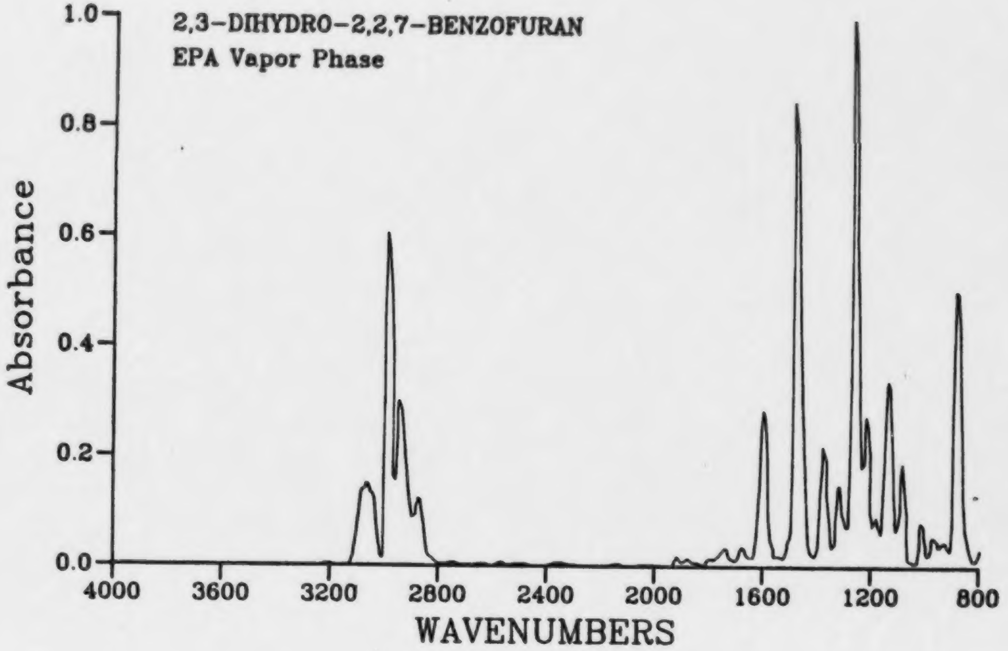


Figure 5.162. Standard EPA Vapor Phase IR Spectrum of 2,3-dihydro-2,2,7-benzofuran.

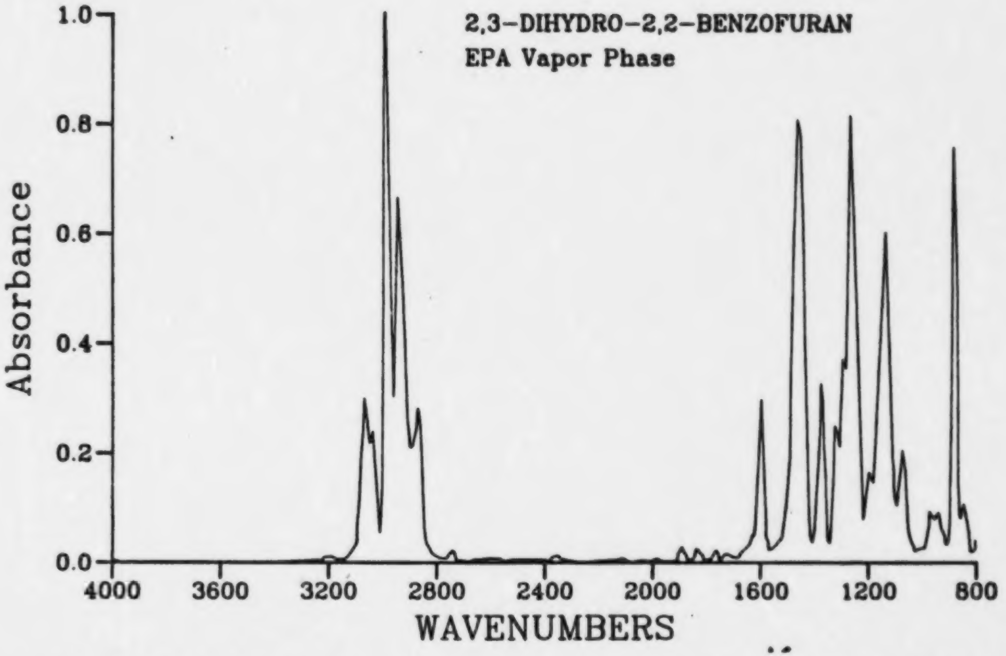
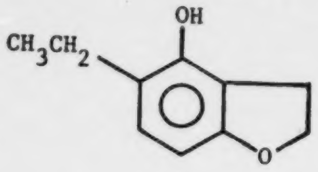


Figure 5.163. Standard EPA Vapor Phase IR Spectrum of 2,3,-dihydro-2,2-benzofuran.

There is a phenolic hydroxy group and an ethyl group on the aromatic ring, and a careful analysis of the FTIR data suggests the following structure for the compound:



(A discussion of the GC/FT-IR data for this analysis has been presented: L. V. Azarraga, D. A. Hanna, J. M. McGuire, D. Betowski, W. Shackelford, New Analytical Capabilities of GC/FT-IR, Pittsburgh Conference, 1980, paper #416.) The availability of this compound as a standard from a commercial source was investigated; the compound is not sold commercially. Custom synthesis was considered in order to produce a standard to confirm the identification but was rejected because of the projected cost ($2000-$3000), as the synthesis is not straightforward.

Extract 11338 (Acid), Organics and Plastics Industry, Raw Water

The packed column chromatogram for extract 11338 (acid) is shown in Figure 5.164. The mass spectrum of the EPA compound of interest is presented in Figure 5.165. The capillary chromatogram of extract 11338 (acid) is shown in Figure 5.166. The mass spectrum obtained from the capillary analysis is presented in Figure 5.167. Several salient features can be noticed immediately from the mass spectrum. A transition of 19 mass units between the molecular ion and the first major fragment is indicative of the presence of fluorine in the molecule. A minor peak representing the loss of 17 mass units is suggestive of the presence of at least one -OH group in the molecule. A loss of 50 mass units ($\underline{m}/\underline{z}$ 112) suggests the presence of a $-CF_2$ unit. The loss of 48 mass units ($\underline{m}/\underline{z}$ 114) probably represents a sequential loss of CO and HF. The molecule therefore contains at least two fluorine atoms and quite probably at least two oxygen atoms. In conjunction with these observations, the accurate mass measurement data produce two possibilities: $C_6H_4O_3F_2$ (error, 5.5 mmu) and $C_3H_5O_4F_3$ (error, 6.7 mmu). The loss of CO would indi-

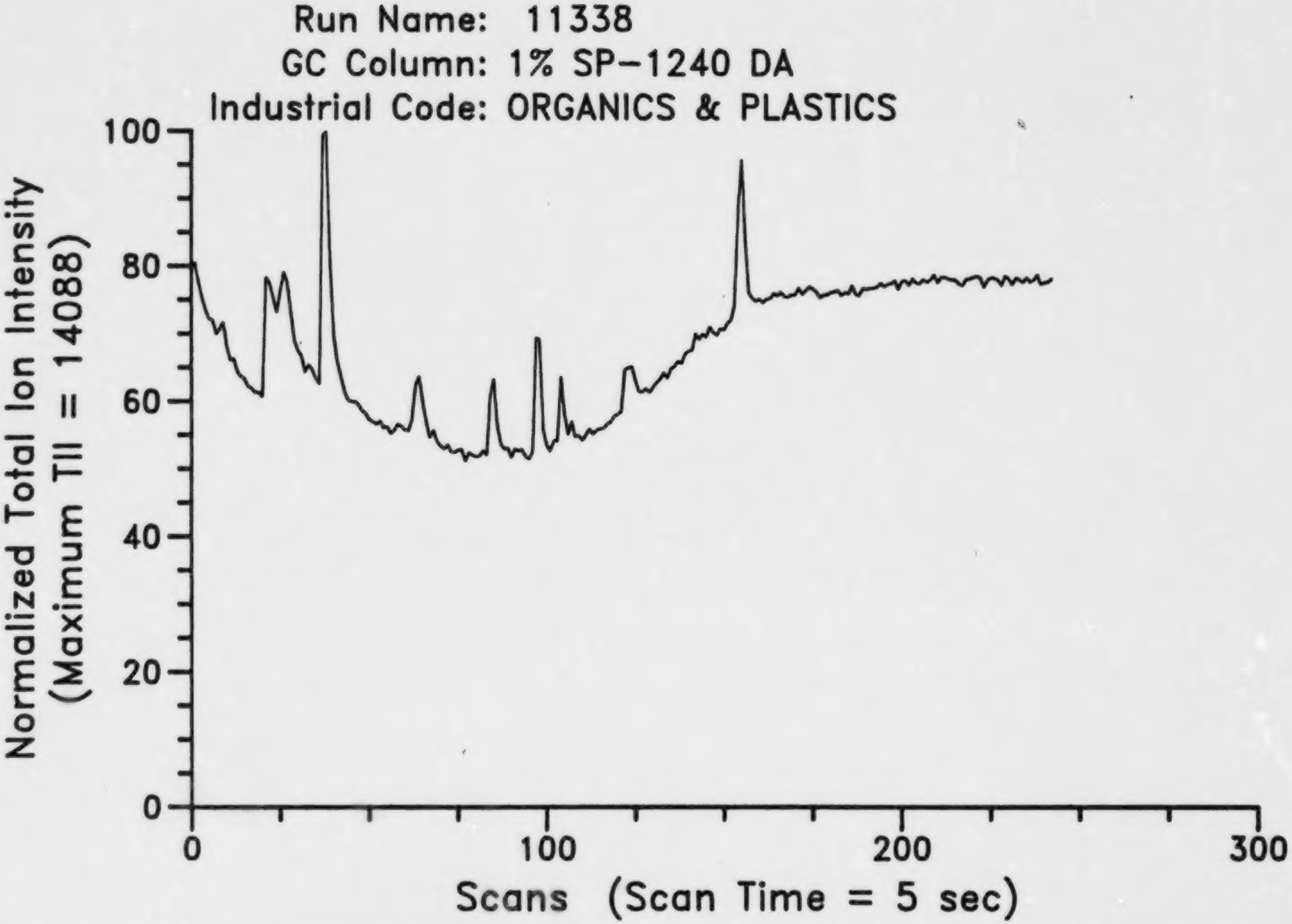


Figure 5.164. Packed column chromatogram of extract 11338 (acid), pesticides manufacturing industry.

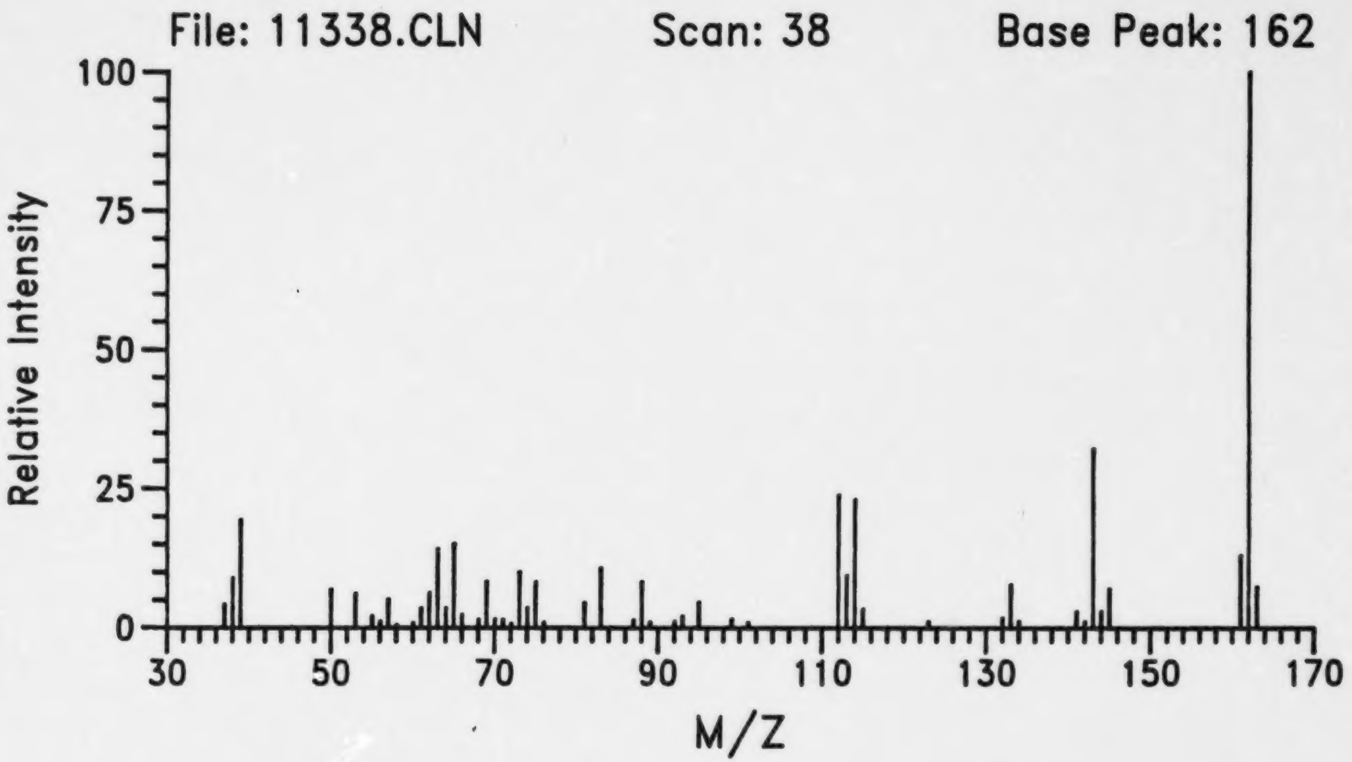


Figure 5.165. Extract 11338 (acid), pesticides manufacturing industry. Frequency of occurrence: 29.

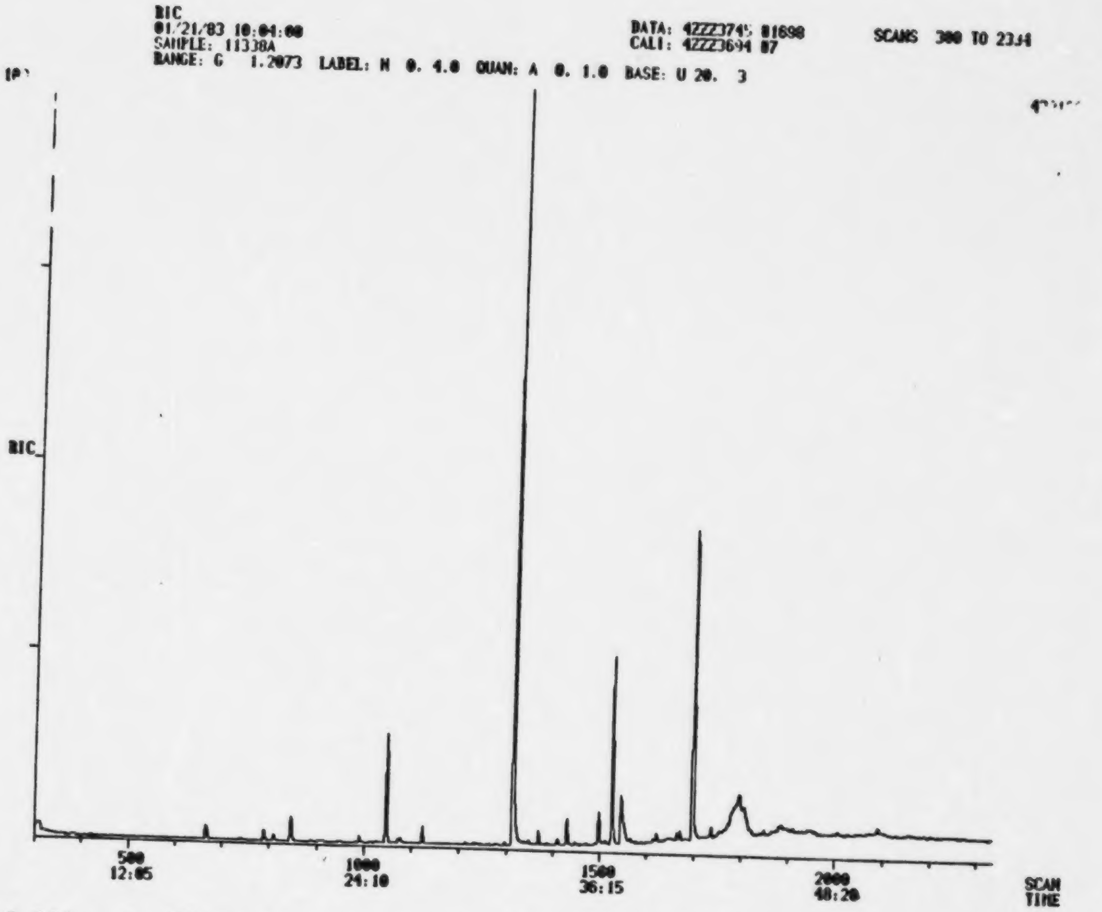


Figure 5.166. Capillary chromatogram, extract 11338 (acid), pesticides manufacturing industry.

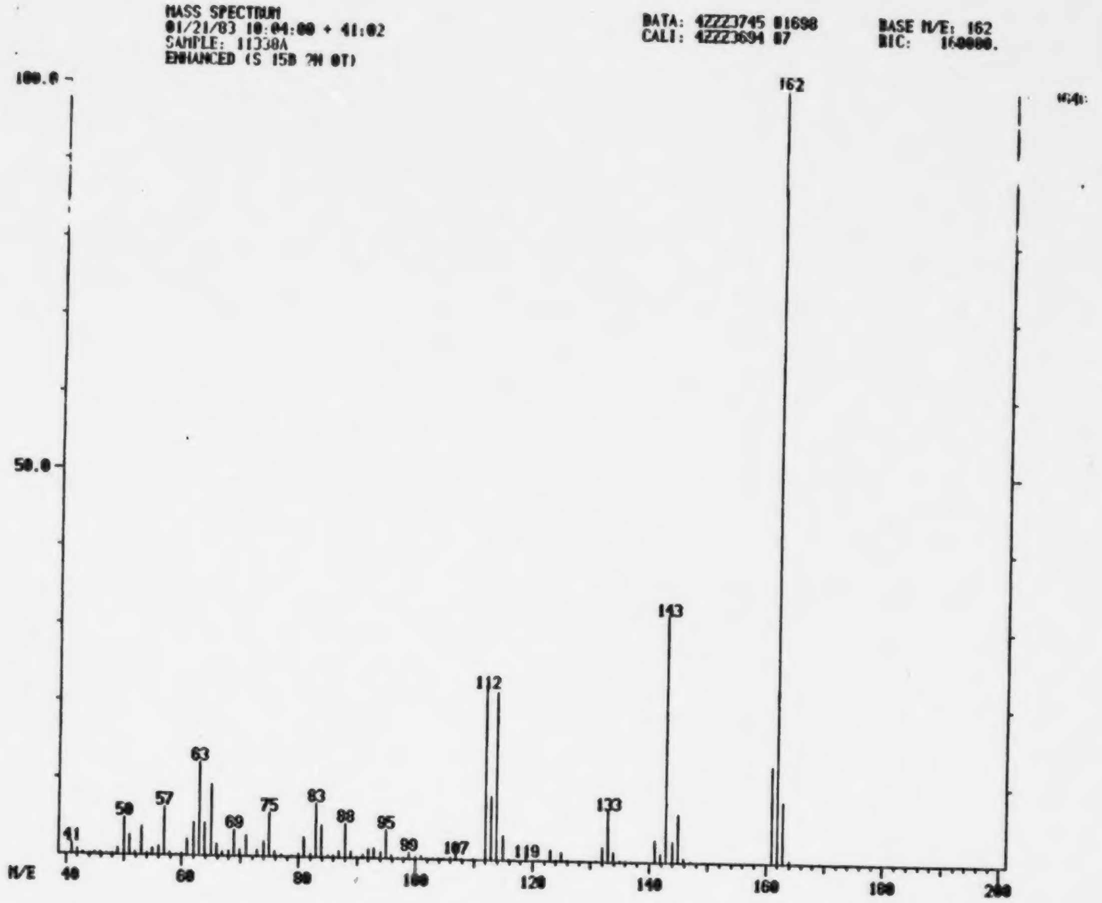


Figure 5.167. Mass spectrum of EPA compound of interest, extract 11338 (acid), pesticides manufacturing industry, scan #1698.

cate that one of the oxygen atoms in the molecule is present originally in a carbonyl group, and this observation would suggest that the possibility with only three carbon atoms is probably only a numerical possibility, not a chemical possibility. Also, there is almost certainly not a $-CF_3$ group present in the molecule, as this moiety always produces an ion of mass 69 in the mass spectrum. The Unacon/FT-IR system was used in an effort to gain information about the nature of the functional groups which contain the oxygen atoms, but the compound of interest was not observed.

Extract 11536 (Base/Neutral), Inorganic Chemicals Industry, Water Supply

The packed column for extract 11536 (base/neutral) is shown in Figure 5.168. The mass spectrum of the EPA compound of interest is presented in Figure 5.169. The capillary chromatogram of extract 11536 (base/neutral) is shown in Figure 5.170. The mass spectrum of the compound of interest as observed in the capillary assay is presented in Figure 5.171. The presence of an ion of mass 129 in the mass spectrum is suggestive of long carbon-chain carboxylic acid, but in the mass spectra of these types of compound, m/z 129 is a low intensity peak (never the base peak of the mass spectrum) and always occurs in combination with a peak at mass 60. Among the ions of the mass spectrum, several transitions involving 17 or 18 mass units are seen, indicating the presence of oxygen. Accurate mass measurement data suggest four possibilities for the ion of mass 259: $C_{18}H_{27}O$ (error, -1.3 mmu), $C_{14}H_{29}O_3N$ (error, 7.2 mmu), $C_{17}H_{27}N_2$ (error, 9.9 mmu), and $C_{13}H_{27}O_3N_2$ (error, 5.4 mmu). Accurate mass measurement for the three other major higher mass ions of the mass spectrum does not show logical transitions among these ions. The conclusion is, therefore, that mass 259 is not the molecular weight. For this reason, the use of chemical ionization mass spectrometry was explored, but the results were inconclusive; no clear indication of a molecular ion species was observed either with methane or with isobutane. The possibilities for compositions obtained from accurate mass measurement can thus not easily be narrowed. If mass 259 is a fragment, it must contain either no nitrogen atoms or two, and possibilities for composition of this ion are narrowed to three. The

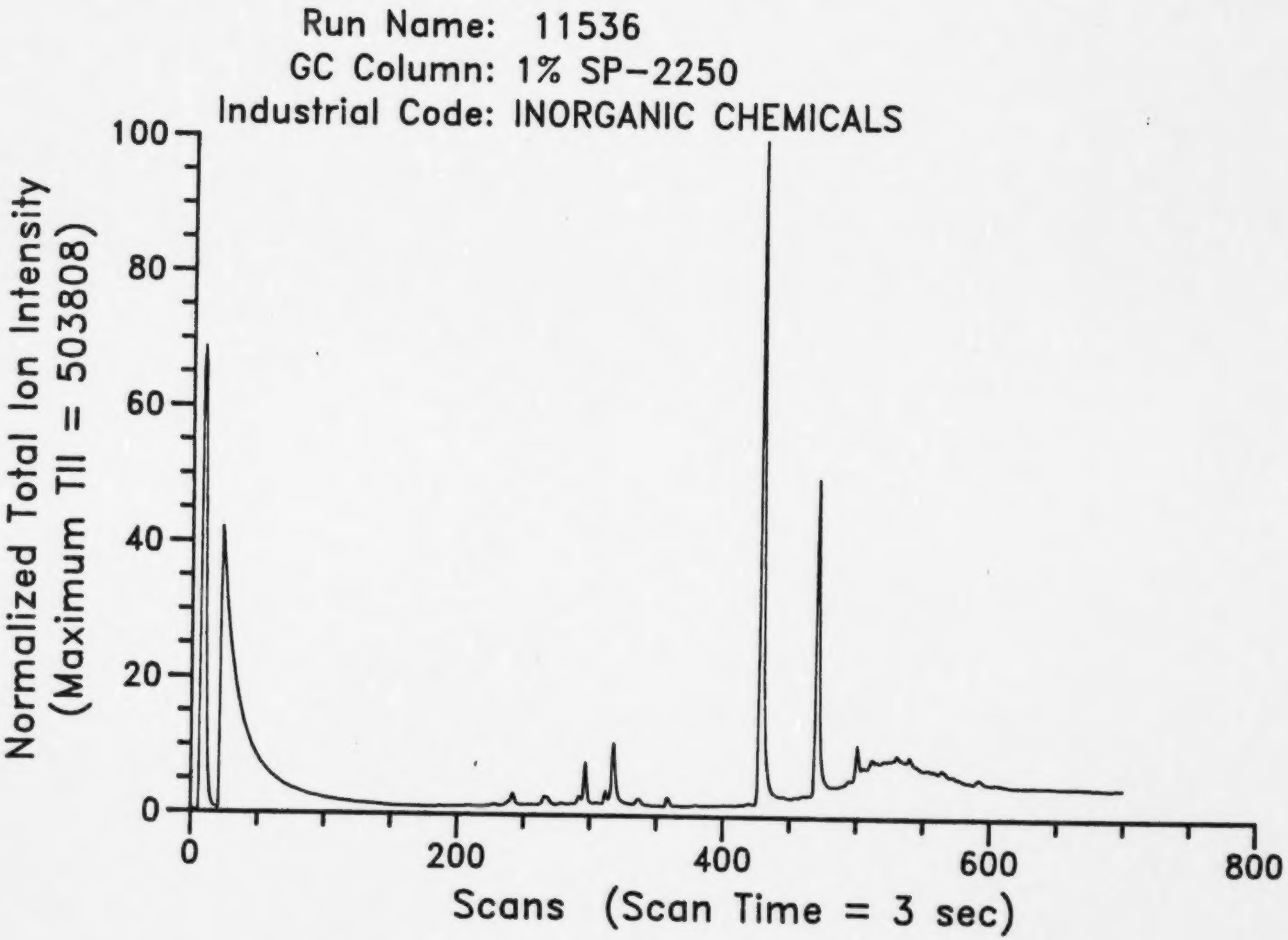


Figure 5.168. Packed column chromatogram, extract 11536 (base/neutral), inorganic chemicals industry.

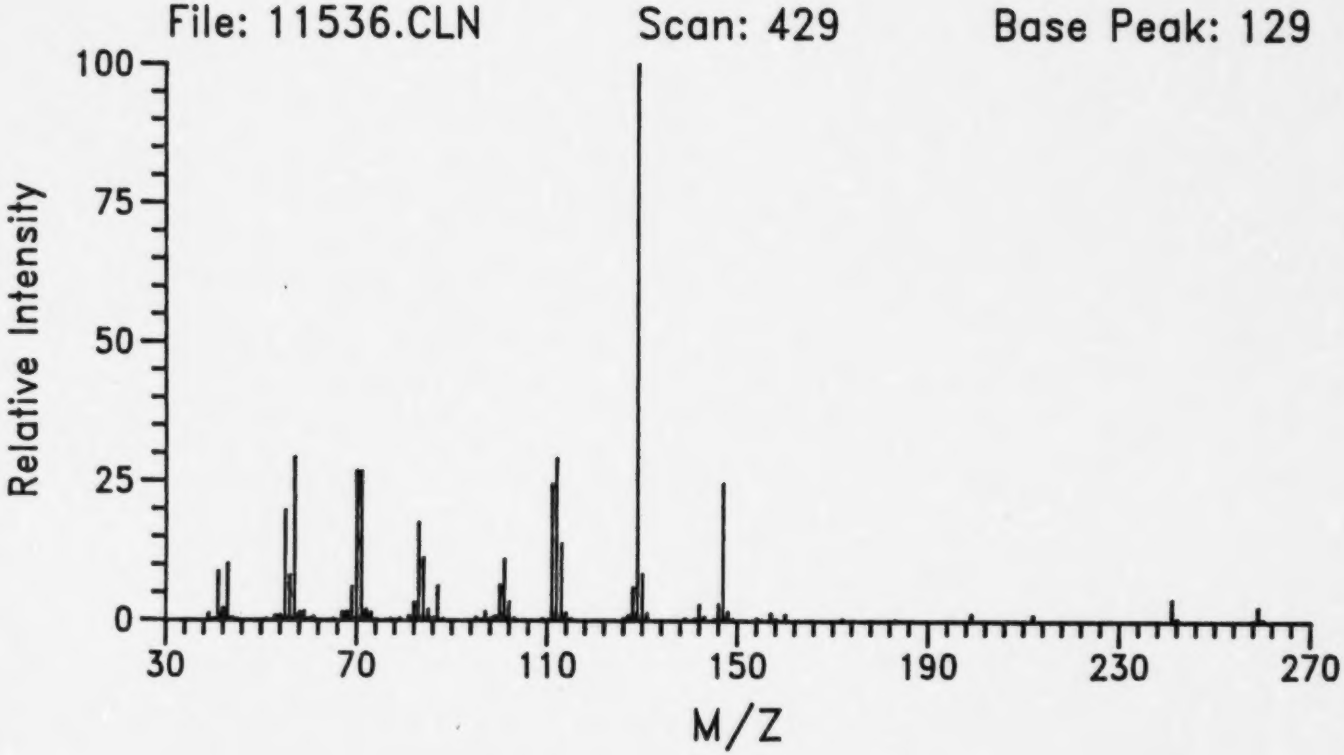


Figure 5.169. Extract 11536 (base/neutral), inorganic chemicals industry.
Frequency of occurrence: 5.

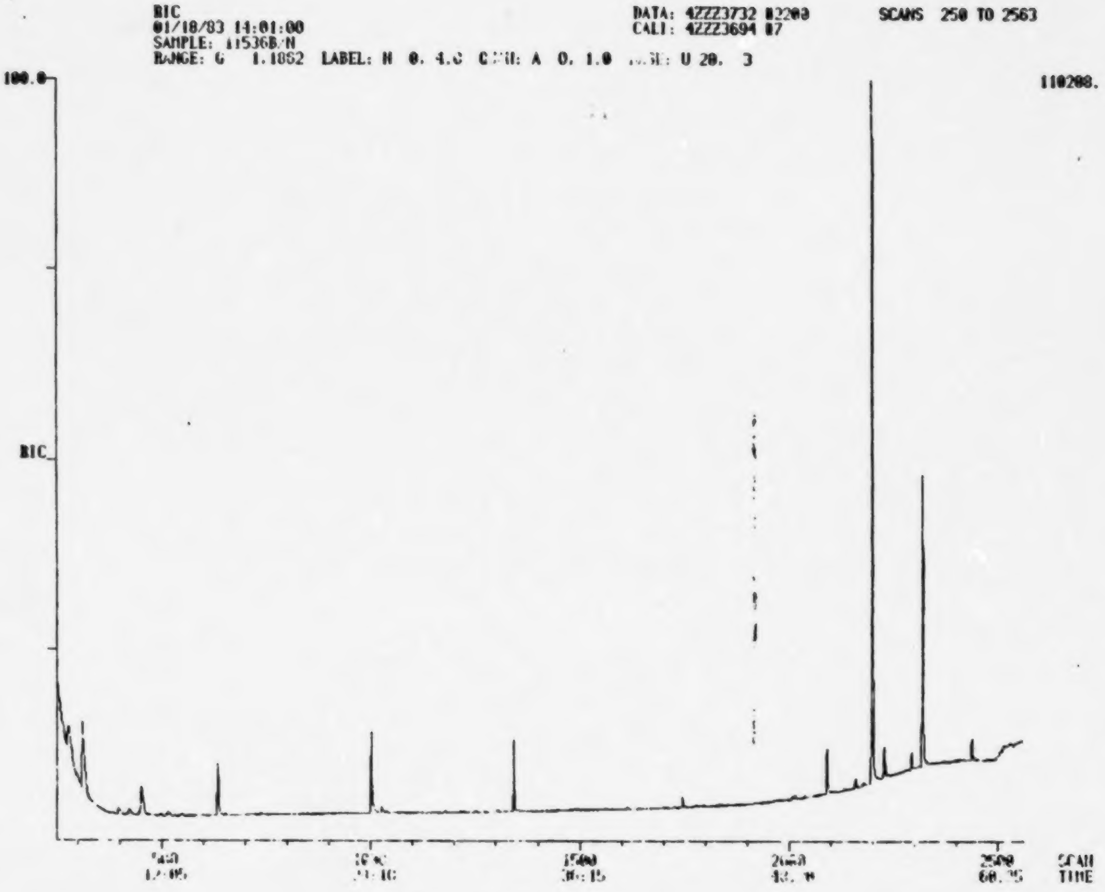


Figure 5.170. Capillary chromatogram, extract 11536 (base/neutral), inorganic chemicals industry.

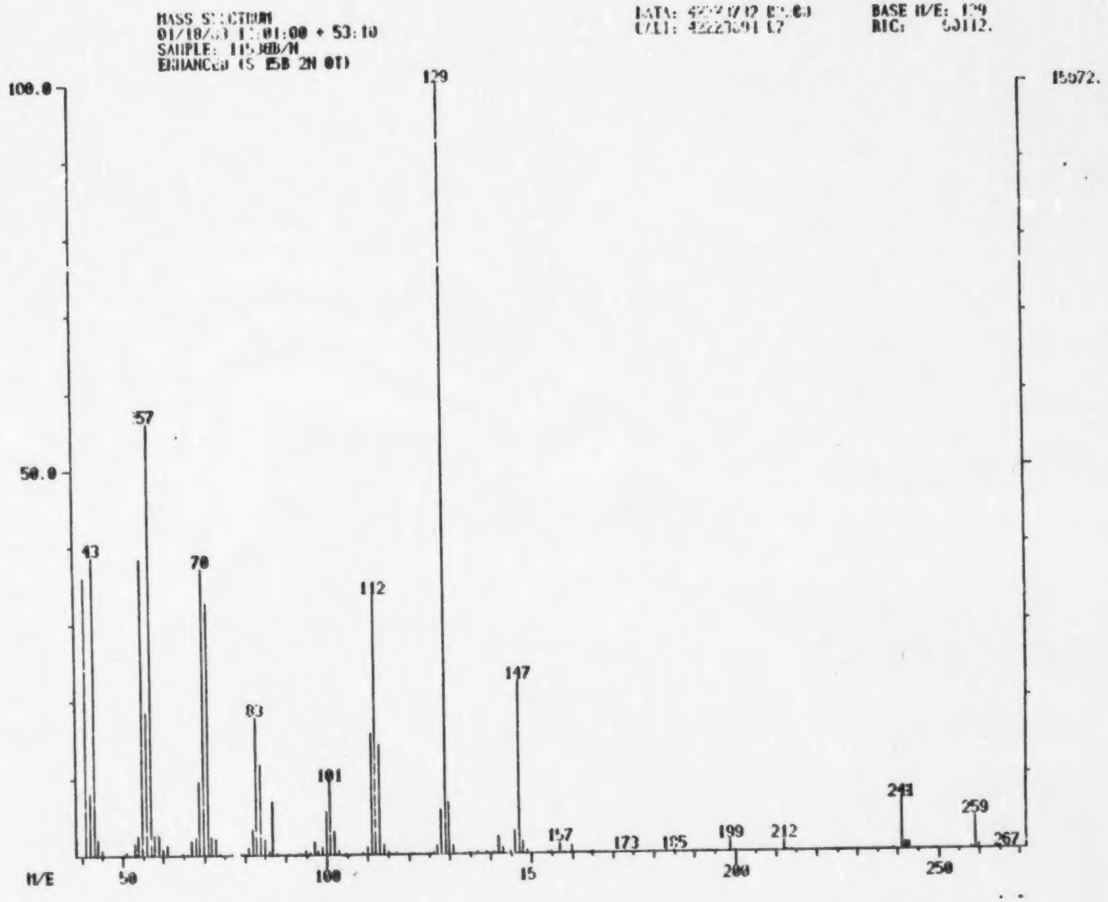


Figure 5.171. Mass spectrum of EPA compound of interest, extract 11536 (base/neutral), inorganic chemicals industry, scan #2200.

possibility which contains no nitrogen also contains only one oxygen atom and, in view of the fact that two transitions which apparently involve loss of water are observed in the mass spectrum, it is very highly probable that more than one oxygen atom should be observed in this fragment. The one remaining possibility for this ion is $C_{13}H_{27}O_3N_2$. In order to obtain a better assessment of the nature of the functional groups, Unacon/capillary GC/FT-IR techniques were applied but the compound of interest was not observed.

Extract 11977 (Base/Neutral), Electronics Industry, Untreated Effluent

The packed column chromatogram of extract 11977 (base/neutral) is presented in Figure 5.172. The mass spectrum of the EPA compound of interest is shown in Figure 5.173. The capillary chromatogram of extract 11977 (base/neutral) is presented in Figure 5.174. The mass spectrum of the EPA compound of interest obtained from the capillary analysis is shown in Figure 5.175. Accurate mass measurement produces only one possibility for the ion of mass 312, $C_{20}H_{40}O_2$ (error, -1.1 mmu). Computerized library search identifies the compound as shown in Figure 5.176, where all possibilities are oxygen-containing and three of the five possibilities are esters. If the compound is assumed to be an ester, a butyl ester becomes a reasonable possibility in view of the fact that $\underline{m}/\underline{z}$ 56 is observed as base peak of the mass spectrum. Starting with pentanoic acid, butyl esters of alkanoic acids show $\underline{m}/\underline{z}$ 56 as either base peak or a major peak. If the compound is a butyl ester and no branching in the alkyl chain is postulated, a tentative identification is butyl palmitate. A reference spectrum of butyl palmitate is contained in the NBS library (Figure 5.177), and an inspection of this reference spectrum perhaps offers a clue as to why the compound was not identified by library search. Although the mass scale of the reference spectrum is printed from mass 10, no peaks are plotted until approximately mass 65. The base peak of the mass spectrum, as obtained from either the packed or capillary column analysis, shows $\underline{m}/\underline{z}$ 56 as base peak. Mass 73 and mass 257 are of approximately the same relative abundance, but that abundance is approximately 25% relative to the base peak, mass 56. Also, the reference spectrum is truncated before a molecular ion at mass

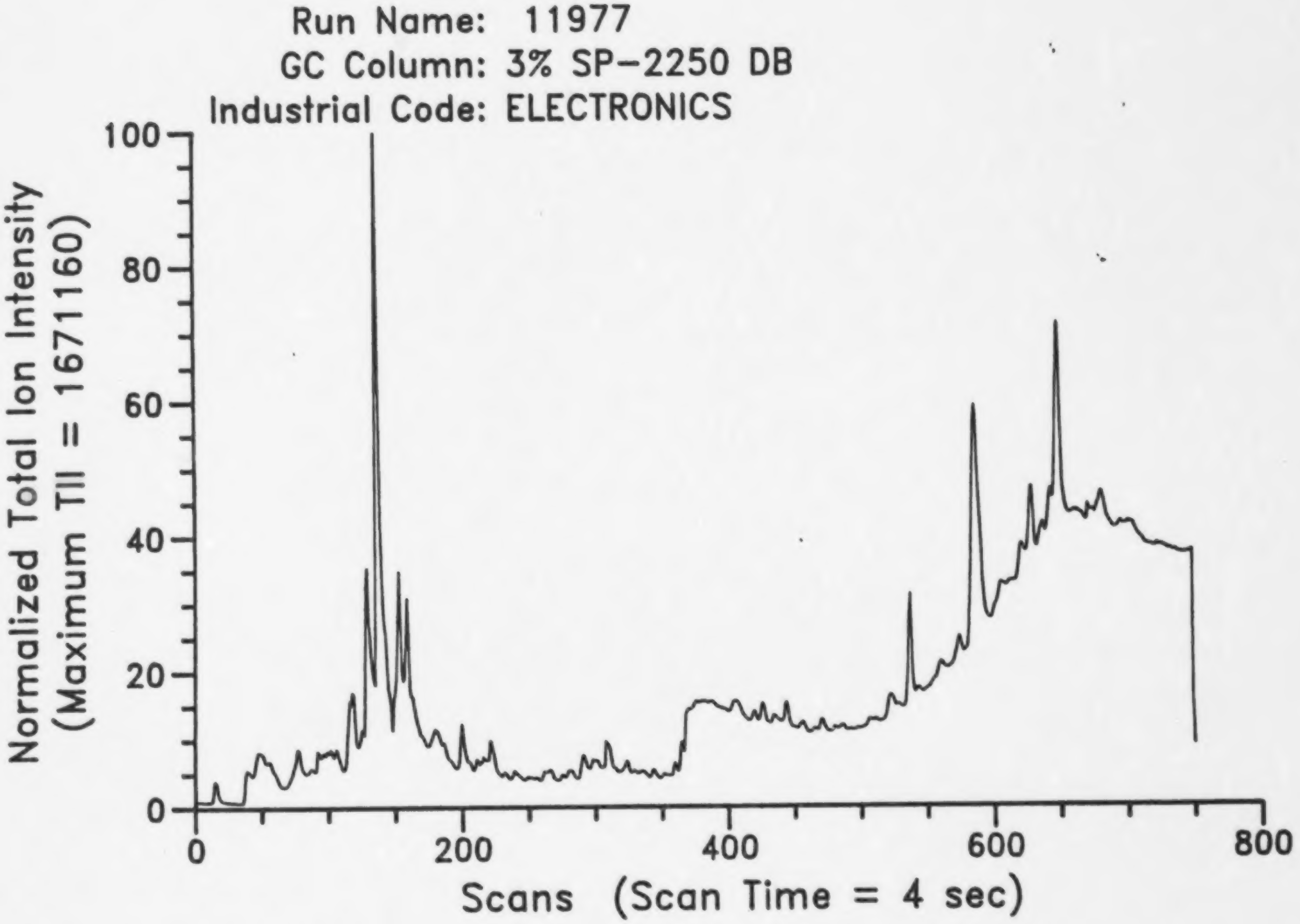


Figure 5.172. Packed column chromatogram, extract 11977 (base/neutral), electronics industry.

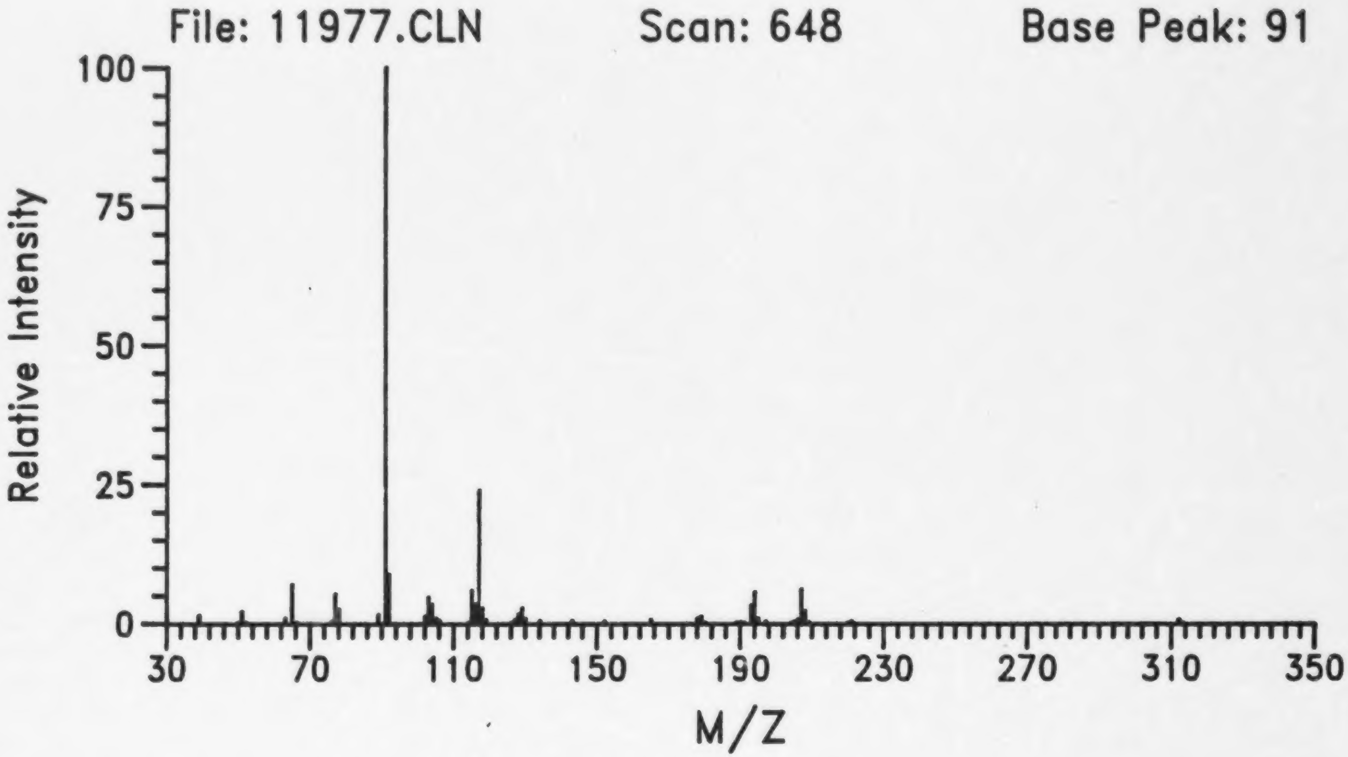


Figure 5.173. Extract 11977 (base/neutral), electronics industry. Frequency of occurrence: 40.

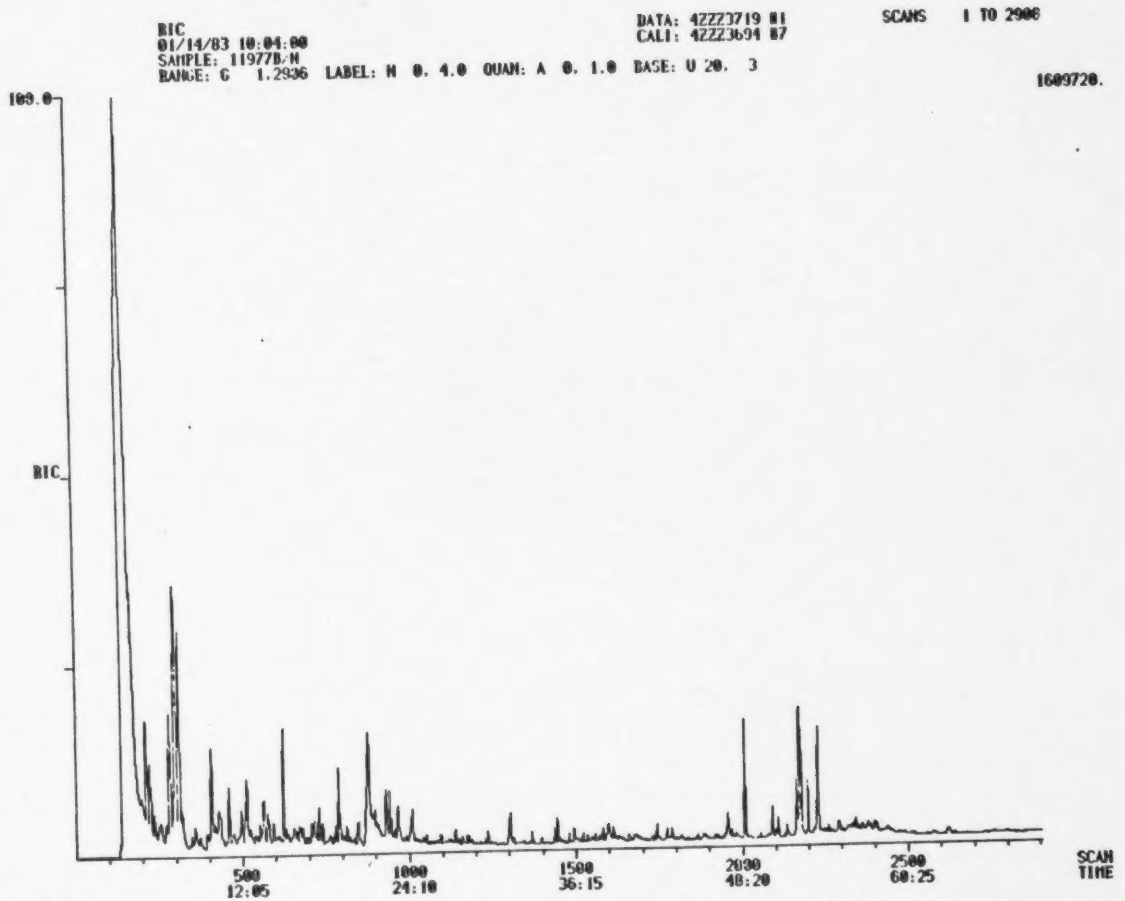


Figure 5.174. Capillary chromatogram, extract 11977 (base/neutral), electronics industry.

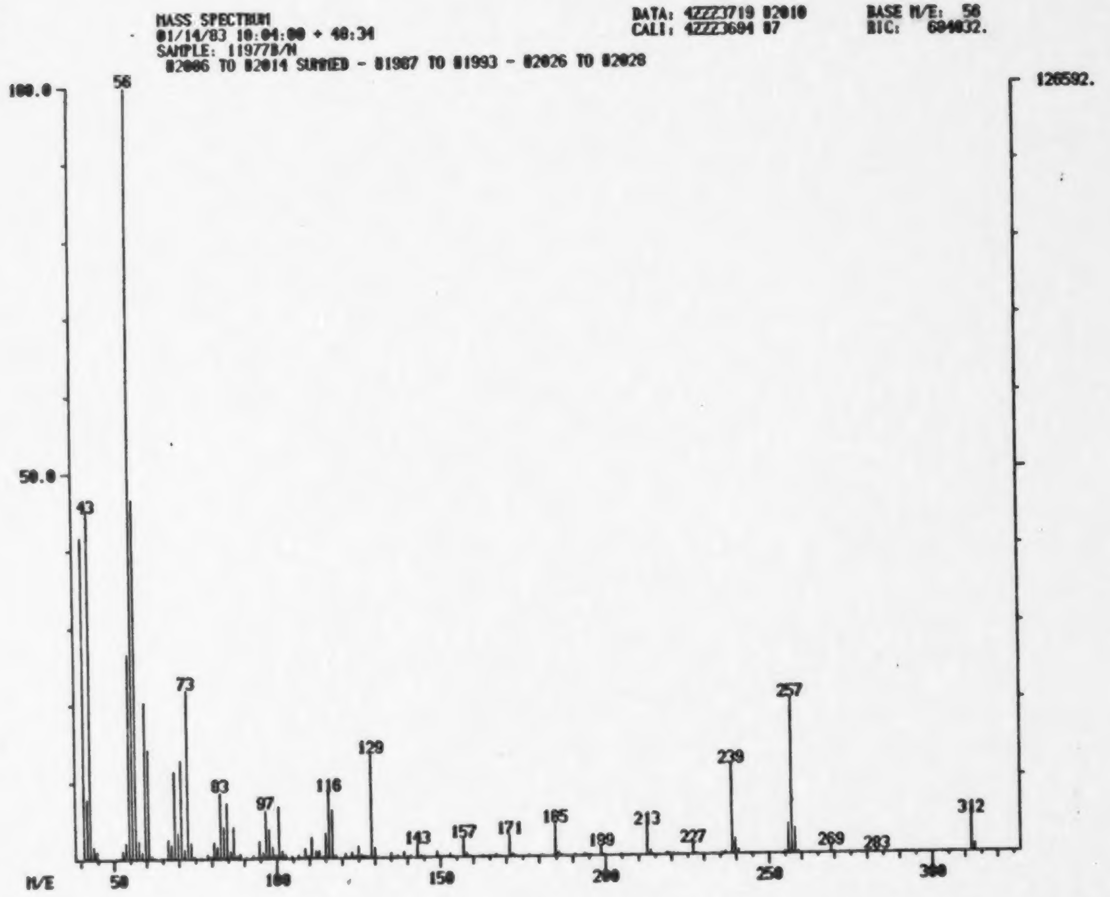


Figure 5.175. Mass spectrum of EPA compound of interest, extract 11977 (base/neutral), electronics industry, scan #2010.

Figure 5.176. Library search, EPA compound of interest, extract 11977 (base/neutral), electronics industry.

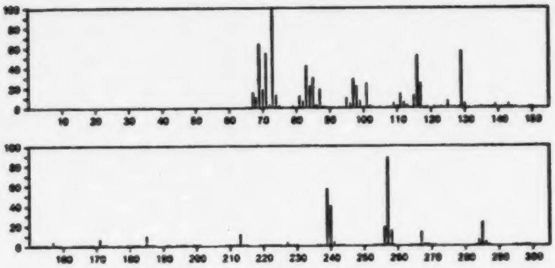
```
LIBRARY SEARCH                  DATA: 4ZZZ3719 *2010       BASE M/E:   56
01/14/83 10:04:00 + 40:34       CALI: 4ZZZ3694 *   7       RIC:    654335.
SAMPLE: 11977B/N
 *2006 TO *2014 SUMMED - *1987 TO *1993 - *2026 TO *2028

25411 SPECTRA IN LIBRARYNB SEARCHED FOR MAXIMUM PURITY
   51 MATCHED AT LEAST 6 OF THE 16 LARGEST PEAKS IN THE UNKNOWN

RANK IN NAME
1  4004 HEXADECANOICACID,1-(HYDROXYMETHYL)-1,2-ETHANEDIYLESTER
2  2518 HEXADECANOICACID,2-HYDROXY-1,3-PROPANEDIYLESTER
3    91 HEXADECANOICACID
4  2556 EICOSANOICACID
5  2781 HEXADECANOICACID,2,3-DIHYDROXYPROPYLESTER

RANK  FORMULA                                 M.WT B.PK   PURITY    FIT   RFIT
1 C35.H68.O5                                   568   43      543    793    604
2 C35.H68.O5                                   568   43      543    787    595
3 C16.H32.O2                                   256   43      492    830    505
4 C20.H40.O2                                   312   43      477    931    493
5 C19.H38.O4                                   330   43      436    669    563
```

Figure 5.177. Reference spectrum, butyl palmitate, from the NBS library.

312 $C_{20}H_{40}O_2$ 111-06-8

Hexadecanoic acid, butyl ester

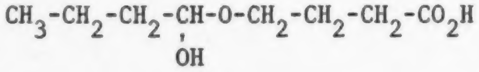
Me(CH$_2$)$_3$OC(O)(CH$_2$)$_{14}$Me



312 can be plotted. Thus, a correspondence to the reference spectrum would be very difficult to establish: the base peak of the spectrum is not plotted and the spectrum is truncated before the molecular ion appears. The search algorithm is not at fault for failing to make the identification; the reference spectrum is poor. In order to confirm the tentative identification, analysis by FT-IR, using the Unacon and capillary gas chromatography was attempted, but the compound of interest was not observed.

Extract 18959 (Acid), Pulp and Paper Industry, Effluent Day 2

The packed column chromatogram for extract 18959 (acid) is shown in Figure 5.178. The mass spectrum of the EPA compound of interest is presented in Figure 5.179. The capillary chromatogram of extract 18959 (acid) is presented in Figure 5.180. The mass spectrum of the EPA compound of interest as obtained from the capillary assay is presented in Figure 5.181. The accurate mass measurement suggests one possibility, $C_8H_{16}O_4$ (error, 4.5 mmu). Chemical ionization (methane), positive and negative detection modes, suggests a molecular weight of 176. A consideration of the salient features of the mass spectrum produces a tentative structure: the presence of an ion of mass 45 suggests the presence of of a carboxy group; the presence of mass 60 supports the assignment of a carboxylic acid unit; the presence of a 57 ion suggests that probably at least four methylene units are attached to each other. Other fragment ions point to the structure below as a tentative assignment.



$$CH_3\text{-}CH_2\text{-}CH_2\text{-}\underset{OH}{\underset{|}{CH}}\text{-}O\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CO_2H$$

The assignment of the structure above is consistent with all available mass spectrometric information, but the interpretation of the mass spectrum, especially without a standard reference spectrum, is always open to some doubt. In order to obtain more information on the nature of the oxygen-containing functional groups, the extract was subjected to analysis by Uncaon/capillary GC/FT-IR, but the compound of interest was not observed. No commercial standard was available for the postulated structure, and custom synthesis was rejected as too expensive.

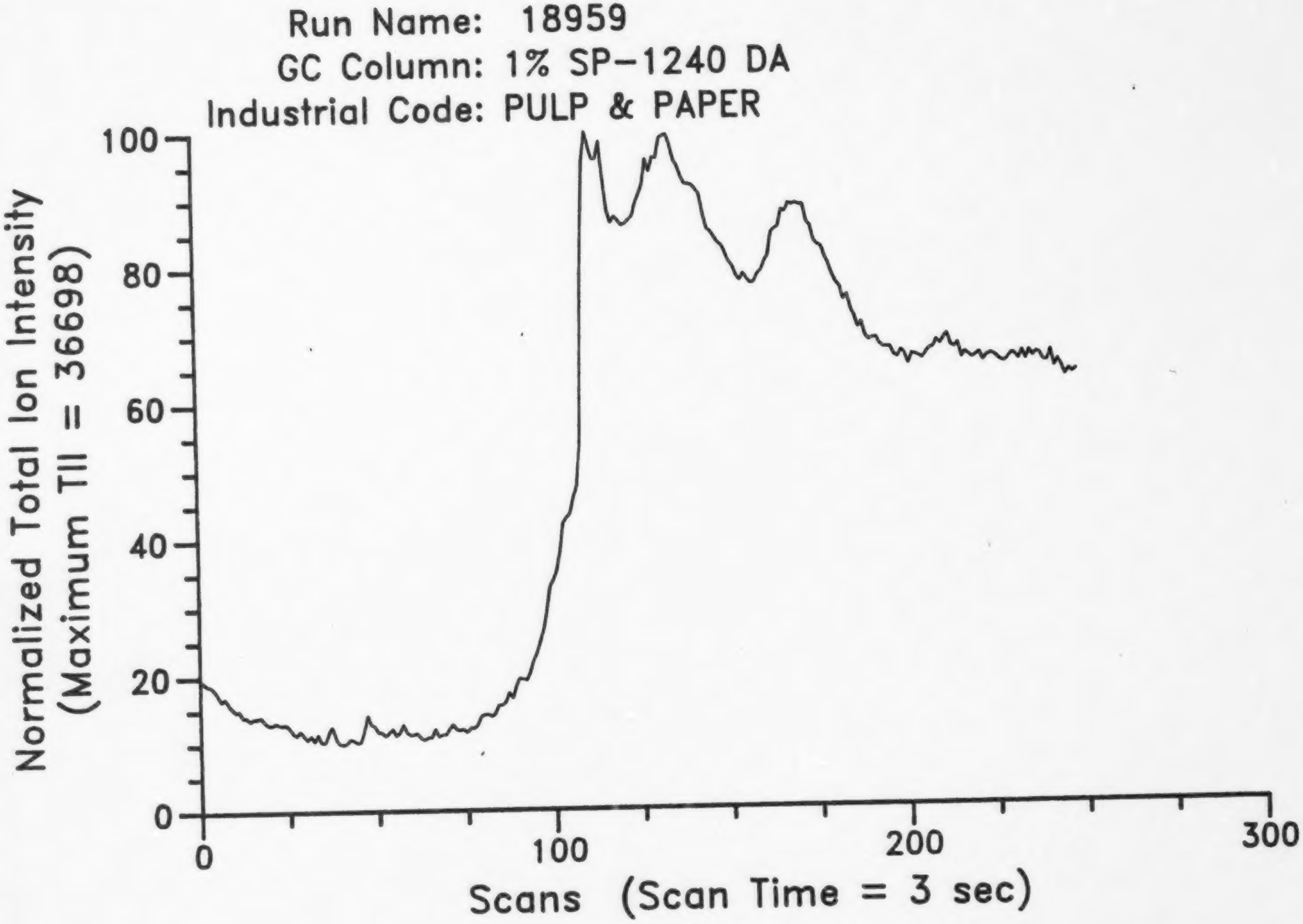


Figure 5.178. Packed column chromatogram of extract 18959 (acid), pulp and paper industry.

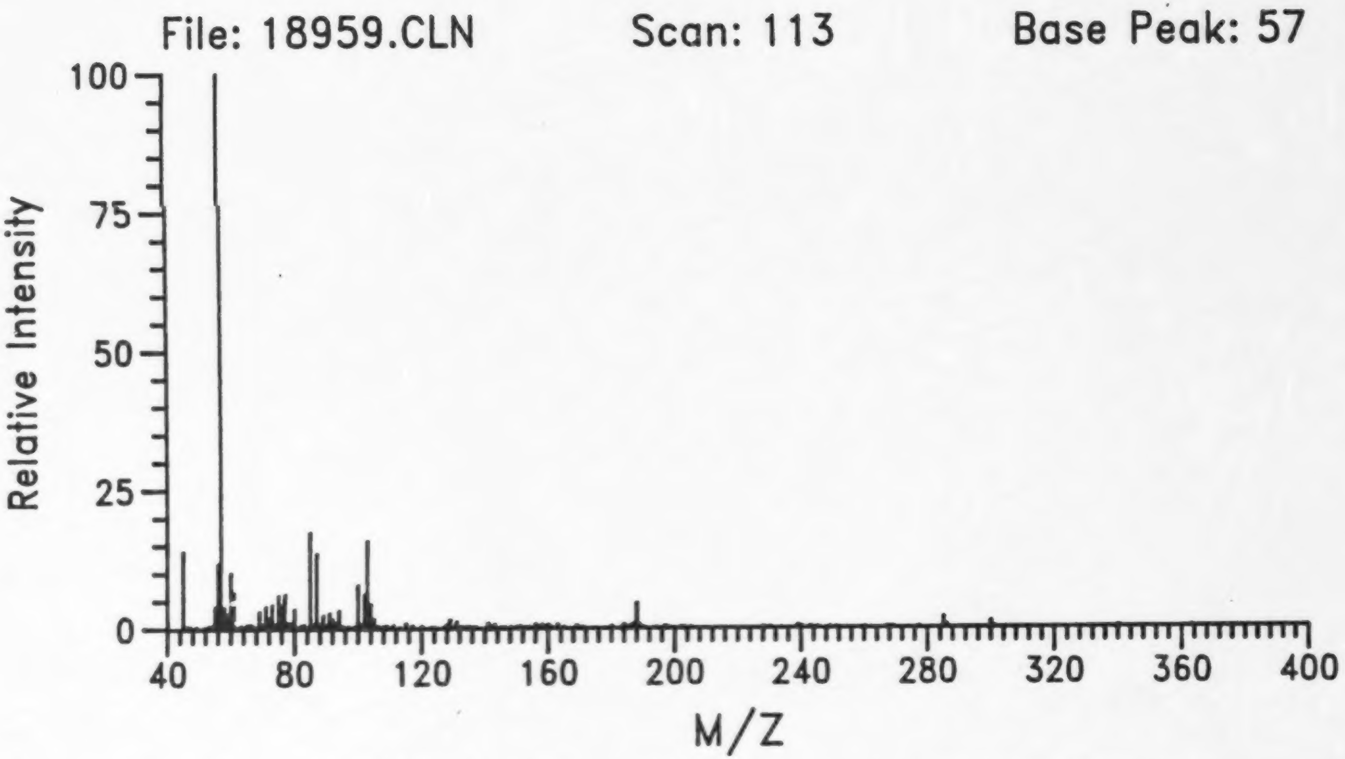


Figure 5.179. Extract 18959 (acid), pulp and paper industry. Frequency of occurrence: 5.

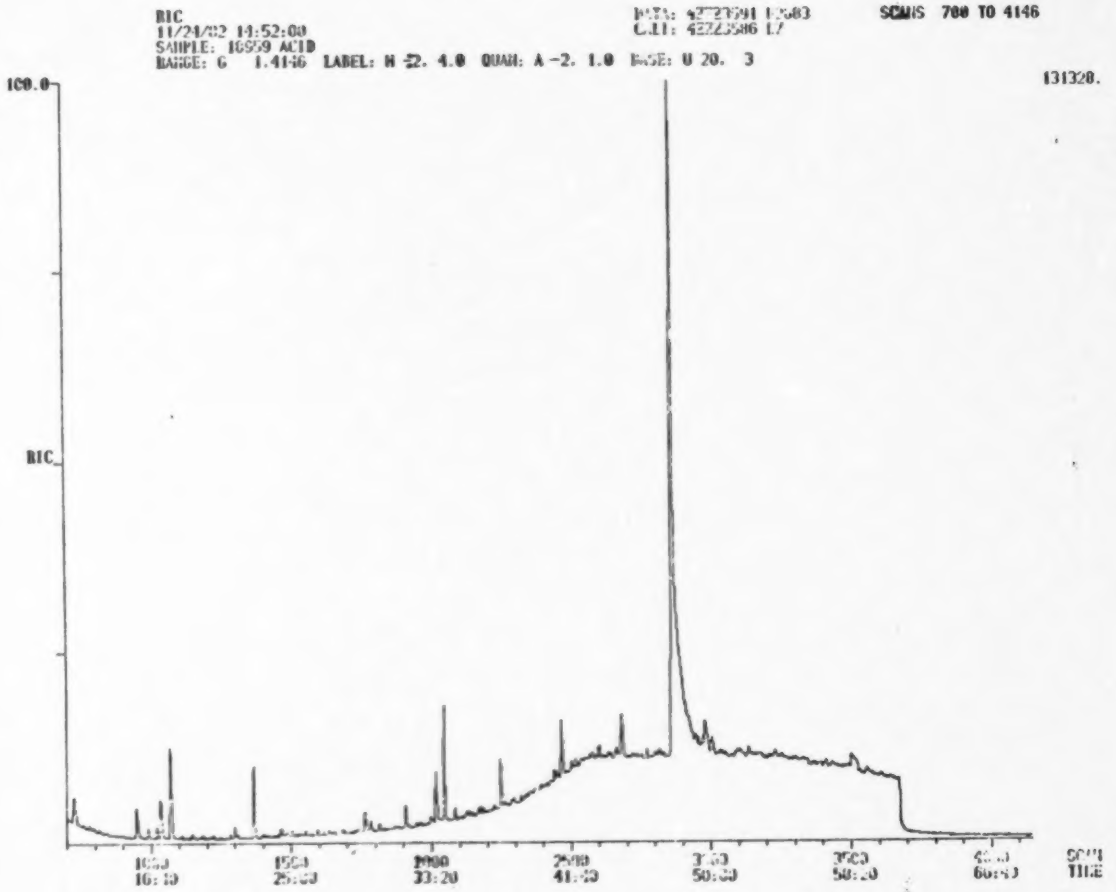


Figure 5.180. Capillary chromatogram, extract 18959 (acid), pulp and paper industry.

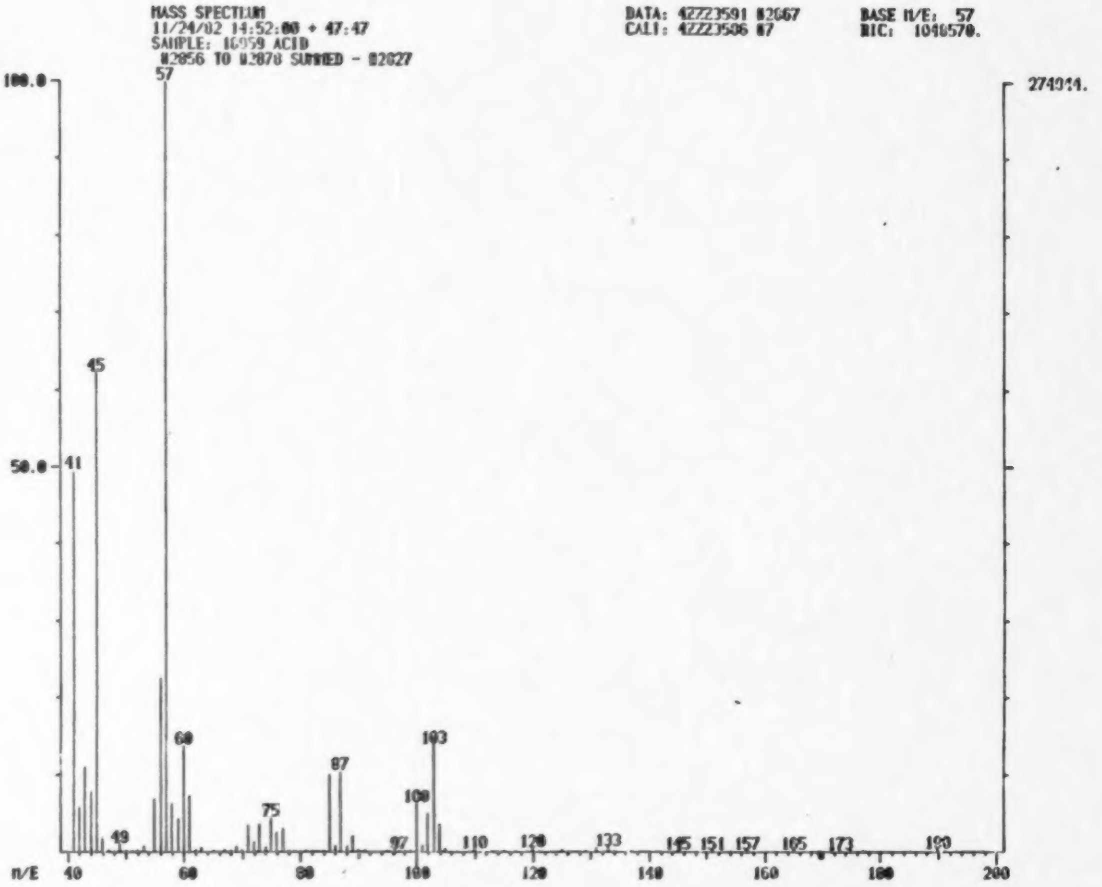


Figure 5.181. Mass spectrum of EPA compound of interest, extract 18959 (acid), pulp and paper industry, scan #2867.

Extract 20250 (Base/Neutral), Explosives Industry, Untreated Effluent-Influent to Treatment

The packed column chromatogram of extract 20250 (base/neutral) is shown in Figure 5.182. The mass spectrum of the EPA compound of interest is presented in Figure 5.183. The capillary chromatogram of extract 20250 (base/neutral) is shown in Figure 5.184. The mass spectrum of the compound of interest as obtained from the capillary chromatogram is presented in Figure 5.185. There is one possibility for the composition of the three major ions of the mass spectrum: mass 268, $C_{15}H_{24}O_4$; mass 148, $C_6H_{12}O_4$; mass 120, $C_4H_8O_4$. The presence of an ion of mass 77 suggests the presence of a benzene ring. Other features of the structure are not readily deduced from the mass spectrum. In an effort to obtain information as to the nature of the functional groups containing the four oxygen atoms, the extract was subjected to analysis by Unacon/capillary GC/FT-IR. The compound of interest was not observed.

Summary

The combined technique of Unacon concentrator/capillary gas chromatography/ Fourier transform infrared spectrophotometry offers great potential for characterization of functional groups. The mass spectra from the extracts in this series demonstrate repeatedly that it is possible to know several properties of a molecule, even an elemental composition, without being able to assign at times even a partial structure. When the GC/FT-IR technique can be applied successfully, the results are all that one might hope for in that a structure can be assigned and there are logical reasons from the data for a preference of one isomer over another. High sample requirements present a difficult problem, however, for the area of environmental analysis. Results obtained from the FT-IR technique were definitely not worth the cost when evaluated on a cost per sample basis for production of useful data.

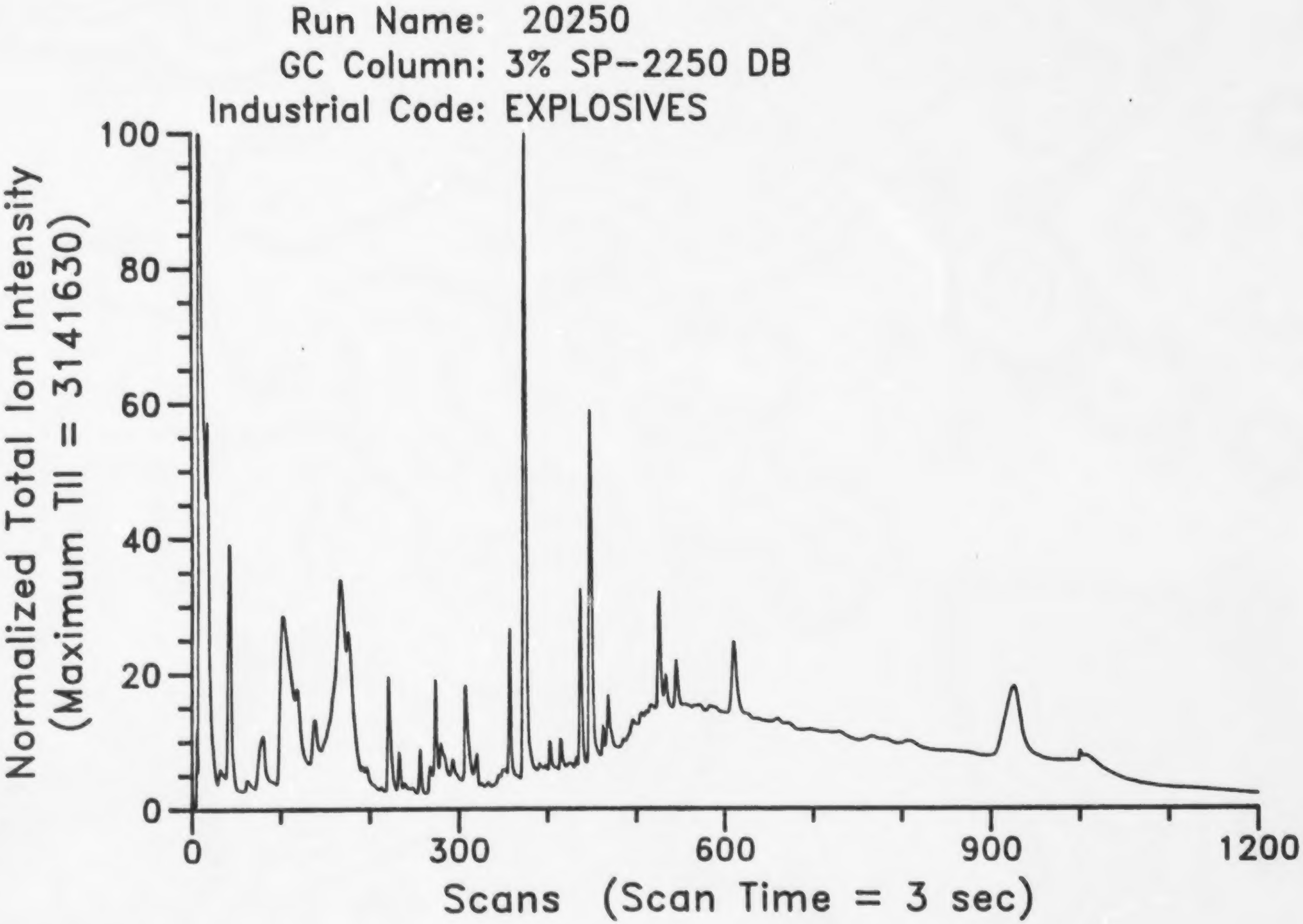


Figure 5.182. Packed column chromatogram, extract 20250 (base/neutral), explosives industry.

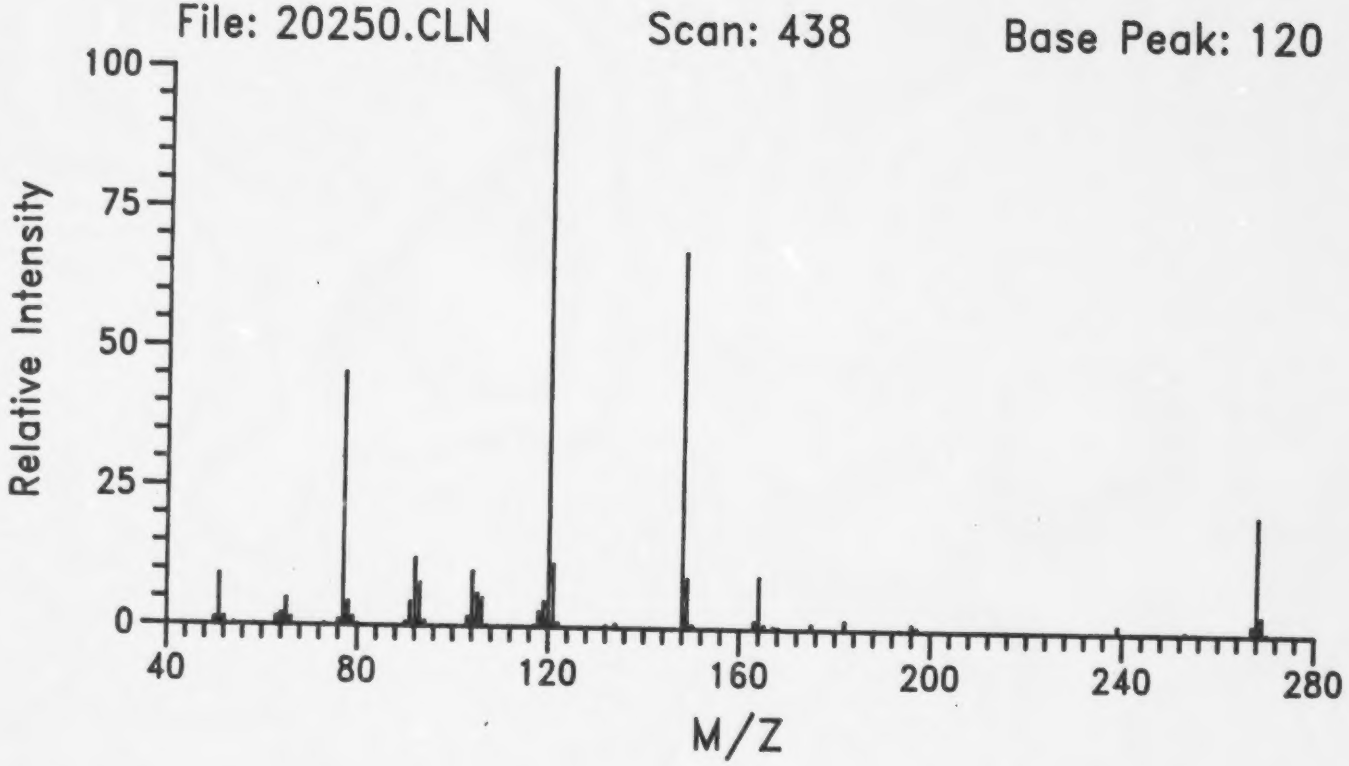


Figure 5.183. Extract 20250 (base/neutral), explosives industry. Frequency of occurrence: 16.

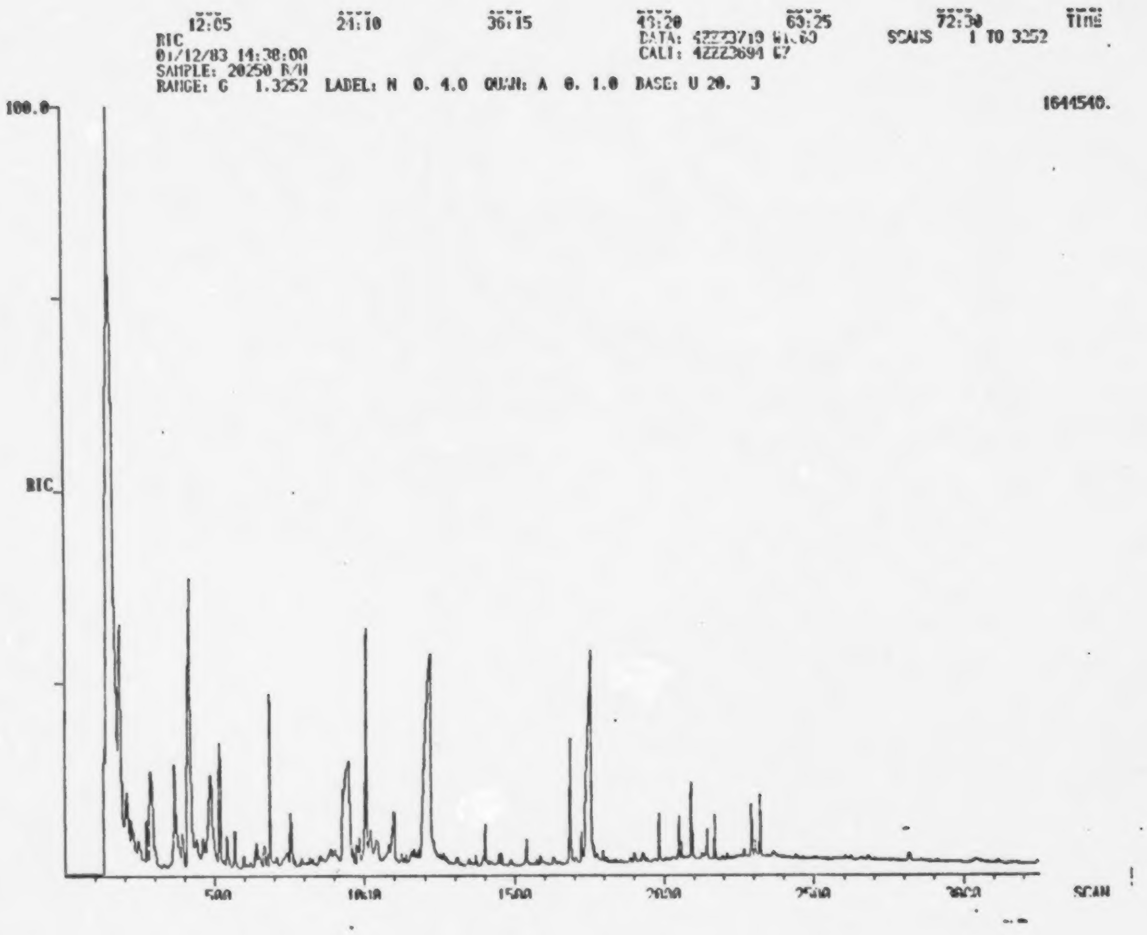


Figure 5.184. Capillary chromatogram, extract 20250 (base/neutral), explosives industry.

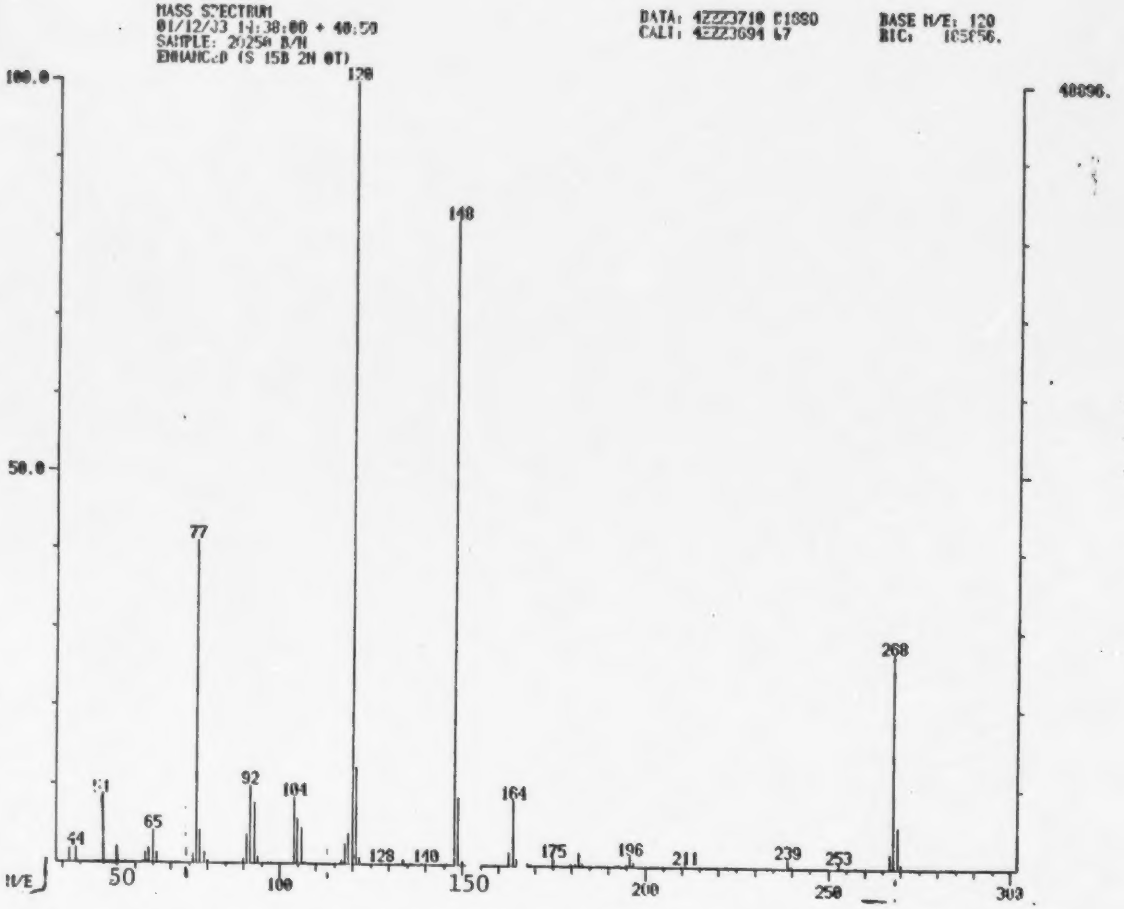


Figure 5.185. Mass spectrum, EPA compound of interest, extract 20250 (base/neutral), explosives industry.

ANALYSES OF REMAINING EXTRACTS

Data for remaining extracts are summarized in Table 5.12. Spectral data and chromatograms are presented in Appendix B, in the following format for each extract: packed column chromatogram, EPA compound(s) of interest, capillary chromatogram, mass spectrum of compound(s) of interest as observed from capillary chromatogram, and Conclusions for each extract.

TABLE 5.12. Summarized data for extracts

Extract	Industry	Analytical Processes Utilized	Conclusions
1634 (acid)	Publicly owned treatment works	Capillary GC/MS analysis	Compound of interest observed.
		Computerized library search	Compound identified as trichloroalkene, with poor fit.
		Chemical ionization (positive and negative) mass spectrometry	No additional information.
		Checked for availability of standards	Very few available; compound not identified by analysis of standards.
			Identification: compound is most probably a 3-4 carbon alkene with 3-5 chlorine atoms.
1678 (acid)	Publicly owned treatment works	Capillary GC/MS analysis	Compound of interest observed.
		Computerized library search	Compound identified as trichloroalkene, with poor fit.
		Chemical ionization (positive and negative) mass spectrometry	No additional information.
		Checked for availability of standards	Very few available; compound not identified by analysis of standards.

(continued)

TABLE 5.12. Summarized data for extracts

Extract	Industry	Analytical Processes Utilized	Conclusions
2389 (acid)	Inorganic chemicals	Capillary GC/MS analysis	Several spectra related to compound of interest obtained Computerized library search inconclusive; does not consistently identify the molecule as chlorinated.
		Accurate mass measurement	Verifies composition as $C_6H_7Cl_3$ for m/z 184.
		Chemical ionization, positive and negative modes	Inconclusive but indicates trichlorocyclohexene isomers and alkylated homologs.
		Checked availability of standards	Trichlorocyclohexenes not available.
2390 (acid)	Inorganic chemicals	Capillary GC/MS analysis	Mandate: search for halogenated compounds, identify if possible.
		Chemical ionization (methane), positive and negative	Compounds usually show more chlorine and carbon than EI spectra but still not necessarily molecular ions/anions; bromo/chloro compounds observed.

(continued)

TABLE 5.12. Summarized data for extracts

Extract	Industry	Analytical Processes Utilized	Conclusions
3005 (base/neutral) 3006 (base/neutral) 3016 (base/neutral)	Porcelain/enameling Porcelain/enameling Pulp and Paper	Capillary GC/MS analysis	Compound of interest observed; same elution time within seconds for both extracts; same spectrum.
		Accurate mass measurement	Either m/z 241 is not a molecular ion or the compound contains nitrogen.
		Chemical ionization (methane), positive and negative modes	Same spectrum observed in negative mode; isotope cluster at 241/243/245 indicates at least 5 chlorine atoms.
4400 (base/neutral)	Auto and other laundries	Capillary GC/MS analysis	Two spectra obtained for compound of interest.
		Chemical ionization mass spectrometry (methane, isobutane)	Compound of interest does not react.
			No structural information.
4752 (base/neutral)	Electronics	Capillary GC/MS analysis	Compound of interest observed.
		Accurate mass measurement	One possibility.
		Chemical ionization mass spectrometry	Peak at $(M+1)^+$ observed.

(continued)

TABLE 5.12. Summarized data for extracts

Extract	Industry	Analytical Processes Utilized	Conclusions
			Tentative structural assignment: indanone isomer.
		Standards purchased, analyzed	Two possible isomers; elution ~ 500 scans earlier than compound of interest.
4809 (acid)	Porcelain/ enameling	Capillary GC/MS analysis	Compound of interest observed.
		Accurate mass measurement	One possibility consistent with chlorine isotope cluster.
		Chemical ionization mass spectrometry	No peaks observed at higher mass than in EI spectrum.
			Composition probably $C_5H_5Cl_5$.
5694 (base/ neutral)	Organic chemicals	Capillary GC/MS analysis	Four spectra corresponding to compound of interest found.
		Accurate mass measurement	Consistent with assignment of structure as a sulfonamide.

(continued)

TABLE 5.12. Summarized data for extracts

Extract	Industry	Analytical Processes Utilized	Conclusions
		Chemical ionization (isobutane)	Shows apparent $(M-1)^+$ species.
		Standards sought	Not available.
5949 (acid)	Pesticides manufacturing	Capillary GC/MS analysis	Compound of interest found.
		Accurate mass measurement	One possibility.
			Very little structural information.
5859 (acid)	Pesticides manufacturing	Capillary GC/MS analysis	Compound of interest found.
		Accurate mass measurement	One possibility; tentative structure.
6057 (acid)	Publicly owned treatment works	Capillary GC/MS analysis	Compound of interest observed.
		Accurate mass measurement	Two possibilities.
			No tentative structure.
8289 (base/ neutral)	Timber products	Capillary GC/MS analysis	Compound of interest observed.
		Accurate mass measurement	One possibility.

(continued)

TABLE 5.12. Summarized data for extracts

Extract	Industry	Analytical Processes Utilized	Conclusions
11722 (acid)	Rubber processing	Capillary GC/MS analysis	Mandate: look for (and identify if possible) brominated compounds.
		Chemical ionization mass spectrometry, positive and negative	Shows more bromine than EI but not molecular species.
11939 (base/ neutral)	Timber products	Capillary GC/MS analysis	Compound of interest found.
		Accurate mass measurement	Nine possibilities for ion of highest mass in EI mass spectrum.
		Chemical ionization mass spectrometry	Inconclusive.
			Conclusion: no definition composition or structure information.
16098 (acid) 16100 (acid)	Publicly owned treatment works	Capillary GC/MS analysis	Compound of interest found; retention time in the two extracts corresponds within 20 seconds.
		Accurate mass measurement	Two possibilities; pentafluorophenol most likely.

(continued)

TABLE 5.12. Summarized data for extracts

Extract	Industry	Analytical Processes Utilized	Conclusions
16217 (base/neutral) 17245 (base/neutral) 19010 (base/neutral)	Publicly owned treatment works Publicly owned treatment works Pharmaceuticals	Capillary GC/MS analysis	Compound of interest observed; same spectrum in all three extracts; retention times agree within a few scans.
		Accurate mass measurement	One possibility; no definite structural assignment.
16683 (acid) 15700 (acid)	Synfuels Pulp and Paper	Capillary GC/MS analysis	Compound of interest observed in both extracts; close correspondence in retention times.
		Accurate mass measurement	One realistic possibility; tentative structure.
20339 (base/neutral)	Timber products	Capillary GC/MS analysis	Compound of interest observed.
		Accurate mass measurement	Four possibilities one most probable.
20435 (acid)	Publicly owned treatment works	Capillary GC/MS analysis	Compound of interest observed.
		Accurate mass measurement	One possibility but ion is not molecular ion.

(continued)

TABLE 5.12. Summarized data for extracts

Extract	Industry	Analytical Processes Utilized	Conclusions
		Chemical ionization mass spectrometry	Inconclusive.
			Conclusion: molecule almost certainly contains at least one more chlorine atom, may also contain more carbon.
20437 (acid) 20474 (acid)	Publicly owned treatment works Nonferrous metals	Capillary GC/MS analysis	Two spectra for compound of interest observed in each extract. Retention times differ by almost 1,000 scans but spectra look the same.
		Chemical ionization mass spectrometry	Inconclusive.